Chapter 1

INTRODUCTION

Conducting polymers have established themselves as an important class of materials with wide range of applications such as electroluminescence devices, non-linear optical materials, oscillators, amplifiers, frequency converters, sensors, EMI shielding, radar absorption etc. Conducting polymers show very interesting properties in electrical and microwave frequencies that make them far more superior to traditional dielectric materials. Non biological materials exhibiting the dielectric properties of biological tissue at microwave frequencies have been used extensively to evaluate hyperthermia applicators, assess microwave imaging systems, to determine electromagnetic absorption patterns and as phantoms.

The microwave and electrical properties and applications of conducting polymers like poly para phenylene diazomethine, polythiophene, polyaniline and Poly (3, 4-ethylenedioxythiophene) (PEDOT) is the subject of this investigation. One of the major drawbacks of conducting polymers is their poor processability, and a solution to overcome this is sought in this investigation. Conducting polymer/thermoplastic composites were prepared by the insitu polymerization method to improve the homogeneity of the composites, probably to a semi IPN level. An important outcome of the work is the development of a processable conducting composite with very good electrical, mechanical and microwave properties and which can be easily solvent cast or coated on various surfaces.
1.1 INTRINSICALLY CONDUCTING POLYMERS

The intrinsically conducting polymers (ICP) have emerged as a new class of materials because of their unique electrical, optical and chemical properties. By proper doping, the conductivity of these materials can be varied from semi conducting to metallic range. Wide and diversified areas of potential applications exist for conducting polymers, such as diodes, battery anodes or cathodes, semiconductors, energy storage and conversion devices, electroluminescence devices, non-linear optical materials, EMI shielding, radar absorbers oscillators, amplifiers, frequency converters, sensors etc. have been reported [1-14].

One of the most exciting areas of research in microelectronics is the development of bio sensing devices. The entrapment of enzymes in conducting polymer films provides a controlled method of localizing biologically active molecules in defined area on the electrodes [6-8]. Probably the most publicized and promising of the current applications are light weight rechargeable batteries. Some prototype cells are comparable to, or better than nickel-cadmium cells now on the market [11]. Microwave properties of conductive polymers finds applications such as coating in reflector antennas, coating in electronic equipments, frequency selective surfaces, EMI materials, satellite communication links, microchip antennas, radar absorbing materials etc [15-18].
1.2 CONJUGATED POLYMERS

Intrinsically conducting polymers are usually extensively conjugated molecules. Conjugated polymers are either insulators or wide-gap semiconductors in their pristine neutral state, and some of them turn into metallic type conductors after a process called doping. The first conjugated polymer, polythiazyl \((SN)\)_x, was discovered in 1975, which possesses metallic conductivity and becomes superconductor at 0.29 K [19].

However, the idea of using polymers for their electrical conducting properties actually emerged in 1977 with the findings of Shirakawa et al. [20], that the iodine doped trans-polyacetylene, \((CH)\)_x, exhibits conductivity of 103 S/cm. Since then, an active interest in synthesizing other organic polymers possessing this property has been initiated. As a result, other conducting polymers having pi-electron conjugated structure, such as polyaniline (PANI), polypyrrole (PPY), polythiophene (PTH), polyfuran (PFU), poly(para phenylene vinylene) and polycarbazole [1,9,20,21] have been synthesized for exploring them in many applications. Figure 1.1 shows the structural formulae of some important conjugated polymers.

It is believed that conjugated polymers possess a spatially delocalized band-like electronic structure [22, 23]. The essential structural characteristic of all conjugated polymers is their quasi-infinite \(\pi\) system extending over a large number of recurring monomer units. This feature results in materials with directional conductivity, strongest along the axis of the chain [24].
1.3 CONDUCTION IN POLYMERS

For conduction to occur, electrons must be excited (e.g. via a collision with a phonon or with a photon or by an electric field) to an empty level where they can propagate through the material. Conduction in polymers has been explained by Mott and Sheng [25-27].

1.3.1 Mott’s hopping conductivity model

Sir Nevill Mott developed a model of electron conduction in amorphous materials using a non-periodic energy potential throughout the volume of the material and can be applied to conducting polymers [25, 26]. Mott assumes that the electron is
going to move or hop to another site less than the distance ‘R’ away. The number of energy states per unit energy per unit volume is given by ‘$N(E)$’, where ‘$E$’ is the energy. Near the Fermi level, the corresponding density of states per unit volume is just ‘$N(E_F)$’. Within a radius ‘$R$’ of the starting point, the numbers of energy states per unit energy near the Fermi energy is given by

$$n(R) = N(E_F) \cdot V(R) = \left(\frac{4\pi}{3}\right)R^3 N(E_F)$$  \hspace{1cm} (1)

If there are ‘$n(R)$’ energy states per unit energy in the volume, then the average energy between the states is the inverse of ‘$n(R)$’

$$\Delta E = \left(\frac{4\pi}{3}\right) R^3 N(E_F)^{-1}$$  \hspace{1cm} (2)

The probability of an electron being thermally excited is proportional to $\exp(-\Delta E/kT)$. However, if an electron travels a long distance, it must tunnel through a much longer effective barrier. The likelihood of tunneling a distance ‘$R$’ decreases exponentially with ‘$R$’ as $\exp(-2\alpha R)$. ‘$1/\alpha$’ is the decay length of the wave function at the starting site and is related to the height of the potential barrier between sites. By combining the likelihood of gaining the energy ‘$\Delta E$’ and of tunneling through the distance ‘$R$’ we can get the likelihood of the electron moving:

$$P \propto \exp(-2\alpha R) \cdot \exp\left(-\frac{\Delta E}{kT}\right)$$  \hspace{1cm} (3)

The probability is maximized (with respect to $R$) when $\delta P/\delta R = 0$
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\[ R = \left( \frac{8}{9} \right) \pi k T \alpha N(E_F) \quad ^\frac{1}{4} \quad (4) \]

Substituting for 'R', we can finally write the expression for the likelihood of hopping to another site as:

\[ P \propto \exp \left( -\frac{B}{T^{1/4}} \right) \quad (5) \]

\[ B = 4 \left( \frac{2}{9\pi} \right) ^\frac{1}{4} \left( 2 \alpha^3 / kN(E_F) \right) \quad (6) \]

Since the conductivity is proportional to the probability of hopping, the conductivity is given by an equation of the form:

\[ \sigma = \sigma_0 \exp \left( -\frac{B}{T^{1/4}} \right) \quad (7) \]

which is known as Mott's T^{-1/4} Law.

1.3.2 Sheng Model: Tunnel junctions between conducting regions

Sheng [27] proposed a model for conduction where large (metallic) conducting regions are separated by tunneling junctions. In Sheng’s model, Johnson noise induces fluctuating voltages across the junctions. The equation for conductivity is given by

\[ \sigma(T) = \sigma_0 \exp \left\{ -\frac{T_1}{T + T_0} \right\} \quad (8) \]

where 'T_0' and 'T_1' are constants. At high temperatures, \( T >> T_0 \), the fluctuations dominate and the conductivity varies as
\[ \sigma(T) = \sigma_0 \exp \left[ - \frac{T_f}{T} \right] \]  \hspace{1cm} (9)

In Sheng's derivation, if a parabolic potential barrier is assumed between conducting regions

\[ \frac{T_f}{T_0} = \left( \frac{\pi}{4} \right) \left( \frac{2}{h} \right) w \left( 2mV_o \right)^{1/2} \]  \hspace{1cm} (10)

and \[ kT_f = 8 \varepsilon_0 (A/w) \left( V_o/e \right)^2 \]  \hspace{1cm} (11)

where 'A' and 'w' are the (averaged) cross-sectional area and distance across the junction, \( V_o \) is the barrier height, 'e' is the electron charge, 'm' is the electron mass, \( \varepsilon_0 \) is the permittivity of free space, and 'h' is Planck's constant. The values of \( V_o \), 'A', and 'w' are experimentally very difficult or impossible to measure. Schimmel et al [28] have offered a simpler phenomenological model with the same form, but a more intuitive definition for 'T_0' and 'T_f'. At high temperatures, the thermal energy is able to overcome the potential barrier and the conductivity will be proportional to \( \exp (-\Delta E/kT) \). Thus, when \( T \gg T_f \)

\[ \exp (-\Delta E/kT) = \exp (-T_f/T) \]  \hspace{1cm} (12)

and

\[ T_f = \Delta E / k \]  \hspace{1cm} (13)

where \( \Delta E \) is just the barrier height \( V_o \). At low temperature (as \( T \) tends to 0), if it is assumed that the conduction is due solely to tunneling, then

\[ \exp (-T_f/T_0) = \exp (- (2/h) \left( 2mV_o \right)^{1/2} w) \]  \hspace{1cm} (14)
where there are now just two parameters \( V_0 \) (the barrier height) and \( w \) (the tunneling distance). And \( m \) is the effective mass of the electron which is roughly the free electron mass.

It is generally agreed that the mechanism of conductivity in these polymers is based on the motion of charged defects within the conjugated framework \([29, 30]\). Oxidation of the polymer initially generates a radical cation with both spin and charge. This species is referred to as a polaron and comprises both the hole site and the structural distortion that accompanies it. This condition is depicted in Figure 2.

The cation and radical form a bound species, since any increase in the distance between them would necessitate the creation of additional higher energy quinoid units. Theoretical treatments \([31, 32]\) have demonstrated that two nearby polarons combine to form the lower energy bipolaron shown in Figure 1.2.

![Figure 1.2 Schematic representations of polaron and bipolaron.](image)

One bipolaron is more stable than two polarons despite the coulombic repulsion of the two ions. Since the defect is simply a boundary between two moieties of equal energy (the infinite conjugation chain on either side) it can migrate in either direction without affecting the energy of the backbone, provided that there is no significant energy barrier to the process. It is this charge carrier mobility that leads to the high conductivity of these polymers.
The conductivity $\sigma$ of a conducting polymer is related to the number of charge carriers $'n'$ and their mobility, $\mu$:

$$\sigma \propto n \mu$$

Because the band gap of conjugated polymers is usually fairly large, $'n'$ is very small under ambient conditions.

### 1.4 CONDUCTION IN MICROWAVE FIELD

At the microscopic level, a material may have several dielectric mechanisms or polarization effects that contribute to its overall permittivity (Figure 1.3) [33].

![Figure 1.3 Frequency responses of dielectric mechanisms](image)

When an electric field is applied to a material, an induced dipole moment connected to the polarisability appears. There are several types of polarization [34]...
• 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.

1.4.1 Orientation (dipolar) polarization

Permanent dipole moments are oriented in a random manner in the absence of an electric field so that no polarization exists. The electric field ‘$E$’ will exercise torque ‘$T$’ on the electric dipole, and the dipole will rotate to align with the electric field causing orientation polarization to occur (Figure 1.4).

![Figure 1.4 Dipole rotation in an electric field](image)

The friction accompanying the orientation of the dipole will contribute to the dielectric losses. The dipole rotation causes a variation in both ‘$\varepsilon'$’ and ‘$\varepsilon''$’ at the relaxation frequency which usually occurs in the microwave region.
1.4.2 Electronic and atomic polarization

Electronic polarization occurs in neutral atoms when an electric field displaces the nucleus with respect to the electrons that surround it. Atomic polarization occurs when adjacent positive and negative ions “stretch” under an applied electric field. The amplitude of the oscillations will be small for any frequency other than the resonant frequency.

1.4.3 Interfacial or space charge polarization

Interfacial or space charge polarization occurs when the motion of migrating charges is impeded. The charges can become trapped within the interfaces of a material. Motion may also be impeded when charges cannot be freely discharged or replaced at the electrodes. The field distortion caused by the accumulation of these charges increases the overall capacitance of a material which appears as an increase in $\varepsilon'$.

1.5 MICROWAVE PROPERTIES

1.5.1 Relaxation time

Relaxation time $\tau$ is the time required for a displaced system aligned in an electric field to return to $1/e$ of its random equilibrium value (or the time required for dipoles to become oriented in an electric field). Constant collisions cause internal friction so that the molecules turn slowly and exponentially approach the final state of orientation polarization with relaxation time constant $\tau$. When the field is switched off, the sequence is reversed and random distribution is restored with the
same time constant. The relaxation frequency $f_c$ is inversely related to relaxation time $\tau$:

$$\tau = \frac{1}{\omega_c} = \frac{1}{2\pi f_c}$$

(15)

1.5.2 Dielectric constant and dielectric loss

The real part of permittivity $\varepsilon'$ is a measure of how much energy from an external electric field is stored in a material. The imaginary part of permittivity $\varepsilon''$ is called the loss factor and is a measure of how dissipative or lossy a material is to an external electric field. At frequencies below relaxation the alternating electric field is slow enough that the dipoles are able to keep pace with the field variations. Because the polarization is able to develop fully, the loss $\varepsilon''$ is directly proportional to the frequency. As the frequency increases, $\varepsilon'$ continues to increase but the storage $\varepsilon'$ begins to decrease due to the phase lag between the dipole alignment and the electric field. Above the relaxation frequency both $\varepsilon''$ and $\varepsilon'$ drop off as the electric field is too fast to influence the dipole rotation and the orientation polarization disappears.

1.5.3 Cole-Cole diagram

The complex permittivity may be shown on a Cole-Cole diagram by plotting the imaginary part $\varepsilon''$ on the vertical axis and the real part $\varepsilon'$ on the horizontal axis with frequency as the independent parameter. A material that has a single relaxation frequency as exhibited by the Debye relation will appear as a semicircle
with its centre lying on the horizontal \( \varepsilon'' = 0 \) axis and the peak of the loss factor occurring at \( 1/\tau \). A material with multiple relaxation frequencies will be a semicircle (symmetric distribution) or an arc (nonsymmetrical distribution) with its centre lying below the horizontal \( \varepsilon'' = 0 \) axis. The curve in Figure 1.5 is a half circle with its centre on the x-axis and its radius. The maximum imaginary part of the dielectric constant \( \varepsilon''_{\text{max}} \) will be equal to the radius. The frequency moves counter clockwise on the curve.

\[
\varepsilon''_{\text{max}} = \frac{\varepsilon_s - \varepsilon_\infty}{2} = 35.8
\]

\( \varepsilon_\infty = 4.9 \)

\( \varepsilon_s = 76.47 \)

Figure 1.5 Cole-Cole diagram of water at 30 °C [33].

1.5.4 Maxwell-Wagner effect

Mixtures of materials with electrically conducting regions that are not in contact with each other (separated by non-conducting regions) exhibit the Maxwell-
Wagner effect at low frequencies. If the charge layers are thin and much smaller than the particle dimensions, the charge responds independently of the charge on nearby particles. At low frequencies the charges have time to accumulate at the borders of the conducting regions causing \( \varepsilon' \) to increase. At higher frequencies the charges do not have time to accumulate and polarization does not occur since the charge displacement is small compared to the dimensions of the conducting region. As the frequency increases, \( \varepsilon'' \) decreases and the losses exhibit the same \( \frac{1}{f} \) slope as observed in normal ionic conductivity [33-37].

1.5.5 Loss tangent

When complex permittivity is drawn as a simple vector diagram, the real and imaginary components are 90° out of phase. The vector sum forms an angle \( \delta \) with the real axis \( \varepsilon' \). The relative “lossiness” of a material is the ratio of the energy lost to the energy stored.

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{1}{Q} = \frac{\text{Energy Lost per Cycle}}{\text{Energy Stored per cycle}} \tag{17}
\]

\( D \) denotes dissipation factor and \( Q \) is quality factor. The loss tangent \( \tan \delta \) is called tan delta, tangent loss or dissipation factor. The loss tangent represents a ratio of the conduction current to the displacement current in a material. The conduction current is the current due to losses in the material. The displacement current is related to the current present if the material were a perfect dielectric [38].
1.5.6 Microwave absorption

This electromagnetic wave can propagate through free space (at the speed of light, \( c = 3 \times 10^8 \text{ m/s} \)) or through materials at slower speed. Consider a flat slab of material (MUT- Material under Test) in space, with a TEM (Transverse Electromagnetic) wave incident on its surface. There will be incident, reflected and transmitted waves. Since the impedance of the wave in the material \( Z \) is different (lower) from the free space impedance \( \eta \) (or \( Z_0 \)) there will be impedance mismatch and this will create the reflected wave. Part of the energy will penetrate the sample. Once in the slab, the wave velocity \( v \), is slower than the speed of light, \( c \). The wavelength \( \lambda_d \) is shorter than the wavelength \( \lambda_0 \) in free space according to the equations below. Since the material will always have some loss, there will be attenuation or insertion loss (Figure 1.6).

\[
Z = \frac{\eta}{\sqrt{\varepsilon_r}}, \quad \eta = Z_0 = \frac{\sqrt{\mu_0}}{\sqrt{\varepsilon_0}} = 120 \pi \\
\lambda_d = \frac{\lambda_0}{\sqrt{\varepsilon_r}}, \quad v = \frac{c}{\sqrt{\varepsilon_r}}
\]

**Figure 1.6 Reflected and transmitted signals from a material under test (MUT).**

Figure 1.7 depicts the relation between the dielectric constant of the Material under Test (MUT) and the reflection coefficient \( |\Gamma| \) for an infinitely long sample (no reflection from the back of the sample is considered). For small values of the
dielectric constant (approximately less than 20), there is a lot of change of the reflection coefficient for a small change of the dielectric constant.

Microwave absorbing materials can be classified in two broad categories, either dielectric or magnetic absorbers. Dielectric absorbers depend on the ohmic loss of energy that can be achieved by loading lossy fillers like carbon, graphite, conducting polymers or metal particles/powder into a polymeric matrix. Magnetic absorbers depend on the magnetic hysteresis effect, which is obtained when particles like ferrites are filled into a polymeric matrix [39-41].

![Figure 1.7 Reflection coefficient Vs. dielectric constant [33].](image)

There are three conditions that result in a minimum microwave reflectivity. The first equation of interest is that describing the reflection coefficient at an interface.
\[ r = \frac{\eta_M - \eta_0}{\eta_M + \eta_0} = \frac{Z_M - Z_0}{Z_M + Z_0} \]  \hspace{1cm} (18)

where \( r \) is the reflection coefficient and \( \eta \) the admittance of the propagating medium (subscript 0 for incident medium or air and M for the substrate). The reflection coefficient falls to zero when \( \eta_M = \eta_0 \), or in other words the material in the layer is impedance matched to the incident medium. The intrinsic impedance of free space is given by

\[ Z_0 = \frac{E}{H} = \frac{\sqrt{\mu_0}}{\sqrt{\varepsilon_0}} \approx 377 \text{ohms} \]  \hspace{1cm} (19)

where \( E \) and \( H \) are the electric and magnetic field vectors and \( \mu_0 \) and \( \varepsilon_0 \) are the permeability and permittivity of free space. Thus a material with an impedance of 377 ohms will not reflect microwaves if the incident medium is free space. Perfect impedance matching can also be realised if the electric permittivity and the magnetic permeability are equal. This gives the second condition that result in a minimum in the reflection coefficient. In this case the expression for \( r \) becomes [38, 39]

\[ r = \frac{\frac{Z_M}{Z_0} - 1}{\frac{Z_M}{Z_0} + 1} \]  \hspace{1cm} (20)

The normalized intrinsic impedance is

\[ \frac{Z_M}{Z_0} = \frac{\sqrt{\mu_r}}{\sqrt{\varepsilon_r}} \]  \hspace{1cm} Where \( \varepsilon_r = \frac{\varepsilon' - i\varepsilon''}{\varepsilon_0} \) and \( \mu_r = \frac{\mu' - i\mu''}{\mu_0} \) \hspace{1cm} (21)
If the incident medium is free space and the reflectivity is zero, then it follows that \( \varepsilon_r^* = \mu_r^* \). The implication is if both the real and imaginary parts of the permittivity and permeability are equal, then the reflectivity coefficient is zero. The third consideration is the attenuation of the wave as it propagates into the absorbing medium. The power of the wave decays exponentially with distance, \( x \), by the factor \( e^{-\alpha x} \) is the attenuation constant of the material and can be expressed as

\[
\alpha = -\sqrt{\varepsilon_0 \mu_0} \omega \left( a^2 + b^2 \right)^{1/4} \sin \left( \frac{1}{2} \tan^{-1} \left( \frac{a}{b} \right) \right)
\]  

(22)

Where \( a = \left( \varepsilon_r^* \mu_r^* - \varepsilon_r^* \mu_r^* \right) \) and \( b = \left( \varepsilon_r^* \mu_r^* + \varepsilon_r^* \mu_r^* \right) \)

To get a large amount of attenuation in a small thickness, \( \alpha \) must be large, which implies that \( \varepsilon_r^*, \mu_r^* \) must be large. It is noted here that this condition must be tempered with the first condition, where large values of permittivity and permeability would result in a large reflection coefficient [39].

Microwave Absorbing Materials are used in

- Airplanes & Ships
- Camouflage Nets & Radar Camouflage
- Electromagnetic Interference Suppression- false echoes from ships own superstructure
- Antenna Performance Enhancement – Side and black lobes

The different types of microwave absorbing materials are given in Figure 1.8.
1.6 MEASUREMENT OF MICROWAVE PROPERTIES

Microwave properties of materials can be evaluated with coaxial probe, transmission line, free space, parallel plate and resonant cavity methods [33, 42-48].

1.6.1 Coaxial probe

The open-ended coaxial probe is a cut off section of transmission line. The properties of the material is measured by immersing the probe into a liquid or touching it to the flat face of a solid (or powder) material. The fields at the probe end "fringe" into the material and change as they come into contact with the material. The reflected signal ($S_{ll}$) can be measured and related to $\varepsilon_r$ [42].
1.6.2 Transmission line

Transmission line methods involve placing the material inside a portion of an enclosed transmission line. The line is usually a section of rectangular waveguide or coaxial line (Figure 1.9). \( \varepsilon_r \) and \( \mu_r \) are computed from the measurement of the reflected signal \((S_{11})\) and transmitted signal \((S_{21})\).

![Rectangular Waveguide and Coaxial Waveguide](image)

Figure 1.9 Transmission line, wave guide and coaxial line methods.

1.6.3 Free space

Free-space methods use antennas to focus microwave energy at or through a slab of material without the need for a test fixture. This method is non-contacting and can be applied to materials to be tested under high temperatures and hostile environments [33].
1.6.4 Parallel plate

The parallel plate capacitor method involves sandwiching a thin sheet of material between two electrodes to form a capacitor. A typical measurement system using the parallel plate method consists of an LCR meter or impedance analyzer and a fixture such as the 16451B dielectric test fixture, which operates up to 30 MHz [33].

1.6.5 Resonant cavities

Resonant cavities are high ‘Q’ structures that resonate at certain frequencies. A piece of sample material affects the centre frequency ‘f’ and quality factor ‘Q’ of the cavity. From these parameters, the complex permittivity ‘\( \varepsilon_r \)’ or permeability ‘\( \mu_r \)’ of the material can be calculated at a single frequency. There are many different types of cavities and methods. Here, the most widely used Cavity Perturbation Method, as described in ASTM 252010 [43-47], is considered.

1.6.6 Cavity perturbation technique

The measurements of permittivity and permeability of the dielectric materials are performed by inserting a small and appropriately shaped sample into a cavity and determining the properties of the sample from the resultant change in the resonant frequency and loaded quality factor of the cavity. The basic idea of the cavity perturbation is the change in the overall geometric configuration of the electromagnetic fields with the insertion of a small sample [43-48].
When a small sample is inserted in a cavity which has an electric field ‘$E_0$’ and magnetic field ‘$H_0$’ in the unperturbed state and the fields in the interior of the sample is ‘$E$’ and ‘$H$’, then for loss less sample, the variation of resonance frequency is given by equation (23) as

$$\frac{f_i - f_0}{f_i} = \int (\Delta \varepsilon E_0 \cdot + \Delta \mu H_0 \cdot) d\tau$$

where $\varepsilon$, $\mu$ are the permittivity and permeability of the medium in the unperturbed cavity. ‘$d\tau$’ is the elementary volume and ‘$\Delta \varepsilon$’ and ‘$\Delta \mu$’ are the changes in the permittivity and permeability due to the introduction of the sample in the cavity [49-51]. Without affecting the generality of Maxwell’s equations, the complex frequency shift due to lossy sample in the cavity is given as

$$-\frac{df^*}{f^*} = \frac{(\varepsilon_r - 1)\varepsilon_0 \int E.E_0 \cdot d\nu + (\mu_r - 1)\mu_0 \int H.H_0 \cdot d\nu}{\int (D_0.E_0 \cdot + B_0.H_0 \cdot) d\nu}$$

where ‘$df^*$’ is the complex frequency shift because the permittivity of practical materials is a complex quantity, so the resonance frequency is also complex. ‘$B_0$’, ‘$H_0$’, ‘$D_0$’ and ‘$E_0$’ are the fields in the unperturbed cavity and ‘$E$’ and ‘$H$’ is the field in the interior of the sample [43, 52].

When a dielectric sample is inserted into the cavity resonator where the maximum perturbation occurs that is at the position of maximum electric field, only the first term in the numerator is significant, since a small change in ‘$\varepsilon_r$’ at a point of zero
electric field or a small change in \( \mu_r \) at a point of zero magnetic field does not change the resonance frequency. Therefore equation (24) can be reduced to

\[
- \frac{df}{f^*} = \frac{(\varepsilon_r - 1) \int_{\nu \gamma} E.E_0^* \max dv}{2 \int_{\nu \gamma} |E|^2 dv} \tag{25}
\]

A sample of complex permittivity \( \varepsilon_r \) is kept at the maximum electric field location of the cavity. The sample is taken as a cylinder with uniform cross sectional area \( s \) and length is greater than the narrow dimension \( b \) so that it will occupy the entire narrow dimension of the cavity. After the introduction of the sample the empty resonant frequency and \( Q \)-factor alter, due to the change in the overall capacitance and conductance of the cavity. Quality factor \( Q \) is given by,

\[
Q = \frac{f}{\Delta f} \tag{26}
\]

Where \( f \) is the resonant frequency and \( \Delta f \) is the corresponding 3 dB bandwidth. If \( f_0 \) and \( Q_0 \) are the resonance frequency and quality factor of the cavity without sample and \( f_s \) and \( Q_s \) all the corresponding parameters of the cavity loaded with the sample. The complex resonant frequency shift is related to measurable quantities [53, 54]. On equating real and imaginary parts of equations (24) and (25) we have

For real part:

\[
- \frac{f_s - f_0}{f_s} = - \frac{(\varepsilon_r - 1) \int_{\nu \gamma} E.E_0^* \max dv}{2 \int_{\nu \gamma} |E_0|^2 dv} \tag{27}
\]

We may assume that \( E = E_0 \) and the value of \( E_0 \) in the TE_{10p} mode is [34-36]
\[ E_0 = E_{0\max} \sin (p\pi z/l) \sin (p\pi z/l) \quad p = 1, 2, 3, \text{ etc.} \quad (28) \]

Where ‘a’ is the broader dimension of the wave guide and ‘l’ is the length of the cavity. Integrating and rearranging the equation (27), we obtain

\[ \varepsilon' = \frac{V_c (f_0^2 - f_s^2)}{4V_s f_s^2} \quad (29) \]

where,

\[ V_c = a \times b \times l \quad (\text{volume of the cavity}), \quad 'V_s' \quad \text{is the volume of the sample and 'r' is the radius and 'h' is the length of the sample.} \]

For Imaginary part:

\[ \frac{1}{2} \left( \frac{1}{Q_s} - \frac{1}{Q_0} \right) = \frac{\varepsilon''}{\int_{V_s} E.E_0^{*} \max dv} \quad (30) \]

Integrating and rearranging the equation (30), we obtain

\[ \left( \frac{1}{Q_s} - \frac{1}{Q_0} \right) \frac{V_c f_0^2}{4V_s f_s^2} = \varepsilon'' \quad (31) \]

where ‘\( Q_s \)’ is the quality factor of cavity with sample and ‘\( Q_0 \)’ is the quality factor without sample. Equation (29) and (31) are the standard form of the expression for dielectric parameters using the perturbation technique [34, 36].
For a dielectric material having non-zero conductivity, we have Maxwell's curl equation

$$\nabla \times H = (\sigma + j\omega \varepsilon)E = (\sigma + \omega \varepsilon^\prime)E + j\omega \varepsilon' E$$

(32)

The loss tangent

$$\tan \delta = \frac{\sigma + \omega \varepsilon''}{\omega \varepsilon'}$$

(33)

When \(\sigma\) is very small, the effective conductivity is reduced to [36].

$$\sigma_e = \omega \varepsilon'' = 2\pi \varepsilon_0 \varepsilon_r''$$

(34)

Cavity Perturbation Method uses a rectangular waveguide with iris-coupled end plates, operating in TE_{10m} mode (Figure 1.10). For a dielectric measurement the sample should be placed in a maximum electric field and for a magnetic measurement, in a maximum magnetic field. If the sample is inserted through a hole in the middle of the waveguide length, then an odd number of half wavelengths \((n = 2k + 1)\) will bring the maximum electric field to the sample location, so that the dielectric properties of the sample can be measured. An even number of half wavelengths \((n = 2k)\) will bring the maximum magnetic field to the sample location and the magnetic properties of the sample can be measured.
\[ \begin{align*}
\varepsilon_r' &= \frac{V_s (f_c - f_s)}{2V_s f_s} + 1 \\
\varepsilon_r'' &= \frac{V_s}{4V_s} \left( \frac{1}{Q_s} - \frac{1}{Q_c} \right)
\end{align*} \]

\( V \) is the volume.
index \( c \) is for the empty cavity.
index \( s \) is for the sample loaded.

**Figure 1.10 Resonant cavity measurements, cavity perturbation method.**

The cavity perturbation method requires a very small sample such that the fields in the cavity are only slightly disturbed to shift the measured resonant frequency and cavity \( Q \). This assumption allows simplifying the theory to use the equations above to calculate the dielectric properties of the material. Figure 1.11 shows measurements of three different samples with this cavity. The three measurements are presented on the same graph for comparison purposes.

The resonant frequency of the empty cavity is \( f_c = 9.9375 \) GHz (for \( \text{TE}_{107} \) mode) and it shifts to a lower frequency when the sample is inserted in the cavity. When the resonator is loaded with a sample, the resonance curve broadens, which results in a lower quality factor \( Q \). On the y-axis of Figure 1.11 is the magnitude of the linear transmission coefficient \( |S_{21}| \). The 8720ES network analyzer is used for these measurements. On the left of the figure is a calculation for the Sample 2, which has a cross section of 0.29 by 0.157 cm [33].
$f_c = 9.9375$ GHz
$V_c = 32.516$ cm$^3$
$Q_c = 2105$

$f_s = 9.901$ GHz
$V_s = 0.046$ cm$^3$
$Q_s = 2029$

$\varepsilon'_r = 2.30 \quad \varepsilon''_r = 0.003$

**Figure 1.11** Cavity perturbation method: graphs of empty cavity and samples [35]

### 1.6.7 Comparison of Methods

Many factors such as accuracy, convenience, and the material shape and form are important in selecting the most appropriate measurement technique. Some of the significant factors to consider are summarized in Figure 1.12.
1.7 MICROWAVE PROPERTIES AND APPLICATIONS OF CONDUCTING COMPOSITES

The study of 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, radar absorbing materials etc. Study of the dielectric loss, conductivity, dielectric constant, and absorption coefficient of these polymers in microwave region will highlight their application in these fields [54-57].
Composite materials comprising micro particles of the environmentally stable conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) have been prepared [58]. Rimili and coworkers have developed Polyaniline (PANI/DEHEPSA) films of high conductivity (5000-6000 S/m) and permittivity of above 6000 over X and S bands. 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 [59]. Microwave conductivity study of regioregular poly (3-hexyl thiophene) [60], MnZn ferrite- PVC composite [61] polyurethane, polystyrene and poly vinyl acetate has been reported [62]. Brosseau and coworkers reported the microwave response (30MHz-14GHz) of carbon black and silica particles embedded in linear low-density polyethylene, and carbon black particles and carbon fibers embedded in an epoxy resin [63].

The development of stealth technologies makes use of several types of technique, essentially the optimization of the shape of the object and the application of materials which absorb radar waves. In the latter case, the utilization of polymers has several advantages both from the point of view of matrix properties, when the materials are obtained by filler dispersion (the case of granular materials), and the possibility of giving the polymer a controlled electronic conductivity [64-72]. Electromagnetic interference behaviour of conducting polyaniline composites in the radio frequency range X, Ku, and Ka bands were studied. The conducting composites made from CSA-doped polyaniline blended with the styrene acrylonitrile host polymer exhibit high conductivities, up to $10^4$ S/m, and therefore are compatible with an electromagnetic shielding application [69].
1.8 POLYAZOMETHINES

Polymeric aldimines or poly (schiff base)s are classes of materials known as polyazomethines. It is understood that, the incorporation of nitrogen atoms into the conjugated molecular chains aids in the thermal stability of these materials [73-75]. The first polyazomethine (polyimine or poly schiff base) has been reported in 1923 as a result of polycondensation of terephthalaldehyde and benzidine [76]. Since then, conjugated aromatic polyazomethines with different moieties on both sides of CH=N group have been reported [77-81].

1.8.1 Synthesis of Polyazomethines

1.8.1.1 Solution polycondensation

Many groups have reported synthesis of polyazomethines by solution polycondensation [77-83]. A polyazomethine ether was synthesized by polycondensation reaction of a single monomer containing nitro as well as hydroxyl group in presence of excess K₂CO₃ in DMAC and toluene solvent system [82].

1.8.1.2 Chemical vapour deposition (CVD)

This process involves co-sublimation of two or more reactive monomers which impinge onto a substrate surface, where they react to form a polymer film has been shown to be an effective and efficient means of producing polyazomethines with high conjugation lengths [84, 85]. Electric-field-assisted CVD (EFCVD) has also been recently used to alter the macroscopic structure of these materials. This
technique is especially applicable to fabricate polymer films for optic and electronic application [86].

1.8.1.3 Oxidative polymerization

Simionescu and co-workers reports a novel method for the synthesis of wholly aromatic polyazomethines by oxidative polymerization of monomers having a preformed azomethine linkage [73]. Thiophene or furan-containing polyazomethines were synthesized by chemical oxidative polymerization with ferric (III) chloride [87].

1.8.2 Modifications

Initial reports described polyazomethines as insoluble and infusible polymers, a situation that would minimize their practical applications. Three strategies were employed to produce polymers with reduced processing temperatures:

(i) modification of the length of the flexible spacer, (ii) alteration of the coaxiality in the mesogenic rigid core especially by using meta substituted monomers and (iii) copolymerisation [88-94].

Another interesting way to modify polyazomethines is by complexation with metal ions (Figure 1.13) [92, 93].
Figure 1.13 Intermolecular complexation with copper salts in Thiénylene-Phenylene polyazomethnine.

Solubility could be affected by modifying polyazomethines to polyazomethine ether (Scheme 1.1) [82] or polyazomethine-urethanes [94].

Scheme 1.1 Synthesis of polyazomethine ether [82].

1.8.3 Applications

Because of wide range of fascinating properties, polyazomethines attracted the attention for applications in many fields, e.g. battery anodes or cathodes, semiconductors, energy storage and conversion devices and in integrated electro-optics for switching, displays, electroluminescence (EL) devices, non linear optical materials etc. [99-102].
1.9 POLYTHIOPHENES

Polythiophenes are also an important class of conjugated polymers which are in general environmentally and thermally stable materials. Pure polythiophene without side chains is neither soluble nor fusible. However side chains which give solubility and fusibility to the polymer can be attached to the repeating unit [103-110]. Polymerization of thiophenes can be carried out in many ways and they have recently been excellently described by R. D. McCullough [107].

1.9.1 Synthesis of Polythiophenes

1.9.1.1 Chemical synthesis of unsubstituted polythiophenes

One of the first chemical preparations of unsubstituted polythiophene (PTH) was reported in 1980 by two groups [108,109]. Both synthesized polythiophene by metal-catalyzed polycondensation of 2,5-dibromothiophene (Scheme 1.2).

\[ X-\text{S}-X \xrightarrow{\text{e.g. Mg or Zn}} \text{Ni}^0 \text{catalyst} \rightarrow \left( S-\text{S} \right)_n \]

\[ X = \text{Cl, Br, or I} \]

Scheme 1.2 Synthesis of polythiophene by polycondensation dehalogenation reaction.

Sugimoto [111] described a very simple and effective synthesis of polythiophene by treating thiophene with FeCl₃ (Scheme 1.3).
Scheme 1.3 Synthesis of polythiophene by oxidative polymerization reaction.

Systematic studies of the polymerization of 2, 5-dihalothiophene have been performed by Yamamoto's group [110-114] and also by others [115-117]. Berlin and coworkers have reported the treatment of thiophene with butyl lithium to give 2, 5-dilithio thiophene that can be polymerized with CuCl₂ [118] to form polythiophenes.

1.9.1.2 Chemical synthesis of polyalkylthiophenes (PATs)

The first chemical synthesis of environmentally stable and soluble poly (3-alkylthiophenes) (PATs) [119] was reported by Elsenbaumer and co-workers in 1985. Very shortly after this report, other groups [120-121] also reported both the chemical and electrochemical preparation of PATs.

1.9.1.3 Metal-catalyzed cross-coupling polymerizations

Polyalkyl thiophenes were prepared by Kumada cross coupling reaction [119] where, 5-diiodo-3-alkylthiophene is treated with one equivalent of Mg in THF, generating a mixture of Grignard species [107,123]. A catalytic amount of Ni(dppp)Cl₂ is then added and the polymer is generated by a halo-Grignard coupling reaction (Scheme 1.4).
1.9.1.4 FeCl₃ method for the polymerization of PATs

Sugimoto et al. [124] reported in 1986 a very simple method to prepare PATs. The monomer, 3-alkylthiophene, is dissolved in chloroform and oxidatively polymerized with FeCl₃ [119,125,126], MoCl₅, or RuCl₃ [111]. The FeCl₃ method does not appear to generate 2, 4-couplings in PATs [107]. The Finnish company; Neste Oy has reported a mechanism of the FeCl₃ synthesis of PATs [127]. The FeCl₃ initiates an oxidation of the alkylthiophene to produce radical centres predominantly at the 2- and 5- positions of thiophene, which propagate to form polymer (Scheme 1.5).
Scheme 1.5 Mechanism of PAT synthesis by FeCl₃ route and the possible regiochemical couplings possible in polyalkyl thiophenes.

1.9.1.5 Electrochemical polymerization

The electrochemical polymerization is usually done by electrochemical oxidation of thiophene on a Pt-coated substrate to obtain a thin uniform film. Pt is selected because it is inert against the polymerization reaction at the relatively high oxidation potential of thiophene. Metallic gold (Au) and silver (Ag) nanowire arrays coated with polythiophene (PTH) films were fabricated by successive electrochemical depositions of PTH and metal into the pores of a micro porous alumina membrane [128].
1.9.2 Regioregular poly alkyl thiophenes (PAT)

It is important to point out that the methods discussed above produce irregular PATs with no regional chemical control. Polymerisation leads to a mixture of four chemically distinct triad regioisomers when 3-substituted (asymmetric) thiophene monomers are employed [129]. Irregularly substituted polythiophenes have structures where unfavourable head-head (H-H) couplings cause a sterically driven twist of thiophene rings, resulting in a loss of conjugation. On the other hand, regioregular, head-to-tail (H-T) poly (3-substituted) thiophene can easily access a low energy planar conformation, leading to highly conjugated polymers. The first synthesis of regioregular head-to-tail coupled poly (3-alkylthiophenes) (PATs) was reported by McCullough and Lowe [130] early in 1992. The PATs synthesized by this method contain ~100% HT-HT couplings.

1.9.3 Applications

Polythiophenes are potential candidates to be used as electrical conductors, nonlinear optical devices, polymer LEDs, electro chromic or smart windows, photoresists, antistatic coatings, sensors, batteries, electromagnetic shielding materials, artificial noses and muscles, solar cells, electrodes, microwave absorbing materials, new types of memory devices, nanoswitches, optical modulators and valves, imaging materials, polymer electronic interconnects, nanoelectronic and optical devices, and transistors [103-106,131-133].
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1.10 POLY (3, 4-ETHYLENEDIOXYTHIOPHENE) - PEDOT

During the second half of the 1980s, scientists at the Bayer AG research laboratories in Germany developed a new polythiophene derivative, poly (3, 4-ethylenedioxythiophene) [134-138], having the backbone structure shown below.

PEDOT was initially found to be an insoluble polymer, yet exhibited some very interesting properties. In addition to a very high conductivity (ca. 300 S/cm), PEDOT was found to be almost transparent in thin, oxidized films and showed a very high stability in the oxidized state [134-139].

1.10.1 Synthesis of Poly (3, 4-Ethylenedioxythiophene)s

The synthesis of PEDOT derivatives can be divided into three different types of polymerization reactions:

a. Oxidative chemical polymerization of the EDOT-based monomers.

b. Electrochemical polymerization of the EDOT-based monomers.

c. Transition metal mediated coupling of dihalo derivatives of EDOT.
1.10.1.1 Oxidative chemical polymerization of the EDOT-based monomers

Chemical polymerization of EDOT derivatives can be carried out using several methods and oxidants [131,152,153]. Another polymerization method of EDOT has been reported by de Leeuw et.al [154] utilizing Fe$_3$(OTs)$_3$ at elevated temperature in combination with imidazole as a base (Scheme 1.6). PEDOT prepared by chemical oxidative method exhibited conductivities of up to 550 S/cm [155-156].

\[
\begin{align*}
\text{Scheme 1.6 Chemical oxidative polymerization of EDOT [154].}
\end{align*}
\]

The third, and most practically useful, polymerization method for EDOT is the so-called BAYTRON P synthesis that was developed at Bayer AG [157-160]. This method utilizes the polymerization of EDOT in an aqueous polyelectrolyte (most commonly PSS) solution using Na$_2$S$_2$O$_8$ as the oxidizing agent. Carrying this reaction out at room temperature results in a dark blue, aqueous PEDOT/PSS dispersion, which is commercially available from Bayer AG under its trade name BAYTRON P (Figure 1.14). An interesting aspect of BAYTRON P is that, after drying, the remaining PEDOT/PSS film is highly conducting, transparent, mechanically durable, and insoluble in any common solvent [140-143] and has found several applications [121,144-151].
1.10.1.2 Electrochemical polymerization of EDOT derivatives

Another especially useful polymerization method utilizes electrochemical oxidation of the electron-rich EDOT-based monomers. This method stands out as it requires only small amounts of monomer, short polymerization times, and can yield both electrode-supported and freestanding films. Electrochemical polymerization results in the formation of a highly transmissive sky-blue, doped PEDOT film at the anode [150,161]. A variety of electrolytes are compatible with EDOT-derivative polymerization, including polyelectrolytes, as was nicely demonstrated by Wernet and co-workers, or using an aqueous micellar medium [162-163].

1.10.1.3 Transition metal mediated coupling of dihalo derivatives of EDOT

Many thiophene-based polymers have been prepared over the years using transition metal catalyzed coupling of activated organometallic derivatives. Yamamoto et al.
recently applied this methodology to the direct formation of neutral PEDOT [144]. Prolonged storage (~2 years) or gentle heating (50-80°C) of crystalline 2, 5-dibromo-3, 4-ethylene dioxy thiophene affords a highly conducting, bromine-doped PEDOT. Using this approach, thin films of PEDOT with conductivity as high as 20 S/cm were fabricated on insulating flexible plastic surfaces [164].

1.10.2 Applications of PEDOT

PEDOT-based polymers are applied in many applications like through-hole plating of printed circuit boards, antistatic coatings for cathode ray tubes to prevent dust attraction, primers for electrostatic spray coating of plastics, hole-injecting layers on ITO substrates for organic electroluminescent devices, transparent electrodes for inorganic electroluminescent devices, sensors, rechargeable batteries, cathode radiation tubes, photodiodes, electro-chromic windows, corrosion protection, and photovoltaic devices. Of utmost importance, these examples show that PEDOT is one of the few organic conducting polymers that have successfully found its way from a laboratory curiosity into multiple technical applications [144,169-178].

1.11 POLYANILINE

Due to its ease of synthesis and processing, environmental stability, relatively high conductivity and cost economics, polyaniline is probably the most industrially important conducting polymer today [179-181]. With the extent of doping polyaniline can have four different oxidation states [182-186] like Leucomeraldine base (LEB), Emeraldine (EB), Emeraldine salt (ES) and Pernigraniline (PNB).
Polyaniline can be synthesized mainly by chemical or electrochemical oxidation of aniline under acidic conditions. The method of synthesis depends on the intended application of the polymer. For bulk production chemical method is preferred whereas for thin films and better patterns, electrochemical method is preferred.

1.11.1 Synthesis of polyanilines

1.11.1.1 Chemical synthesis

The conventional method of synthesis of emeraldine salt is the emulsion polymerization of aniline monomer in aqueous media in presence of a mineral acid like HCl [181, 187-190]. An oxidant like ammonium per sulphate or potassium dichromate can be used to initiate the reaction [191-193]. The ideal molar ratio of monomer to acid to oxidizing agent is proved to be 1:1:1 [194, 195]. The aniline salt of protonic acid in the protonic acid medium is mixed with aqueous solution of ammonium per sulphate with a continuous stirring for 4 hrs. The precipitate obtained is then filtered and washed with distilled water so as to obtain emeraldine salt. The principle function of the oxidant is to withdraw a proton from the aniline monomer.

1.11.1.2 Electrochemical synthesis

Electrochemical polymerization is a radical combination reaction and is diffusion controlled. The anodic oxidative polymerization is the preferable method to obtain a clean and better-ordered polymer as a thin film. Electrochemical synthesis is achieved by:
1. Galvanostatic method
2. Potentiostatic method
3. Potential sweep method

Electrochemical reaction is carried out by dissolving 0.1 mole of protonic acid in distilled water at platinum electrode. The first step in the oxidation of aniline is the formation of a radical cation, which is independent of pH. Mohilner et al. [196] classified the oxidation of aniline as an ECE reaction (a succession of rapid electrochemical–chemical–electrochemical reactions). The colour changes observed with polyaniline are yellow (−0.2 V), blue (0.0 V) and green (0.65 V), which are associated with different oxidation states (doping levels).

1.11.2 Applications

PANI's conductivity can be reversibly controlled either electrochemically (by oxidation–reduction) or chemically (by protonation/ deprotonation), and conductivity increases with doping from the undoped insulating base form to fully doped conducting acid form. PANI with different forms find different uses like leucoemeraldine — the completely reduced form find applications in electrochromic devices and in Li–PANI batteries; perningraniline is used for nonlinear optics while emeraldine base consisting of 50% reduced and 50% oxidised moieties is used in HCl sensors and for making thin films. Other applications of conducting PANI include electrostatic charge dissipation, electromagnetic interference, anticorrosion coating, light emitting diodes and batteries. Recently the protonation of PANI with organic sulphonlic acids and macromolecules has been reported for the preparation of electrically conducting polymers with improved processability [184–187] for making conductive blends and composites for various applications. While Shacklette et al. [188] have developed a surface–core doping process in which PANI is predominately doped with one acid at the core of a particle and a second dopant predominately at the surface just to achieve increased
compatibility between the PANI particles and a second polymer matrix e.g. Nylon, polystyrene (PS), low density polyethylene (LDPE).

1.12 DESIGN OF EXPERIMENTS (DOE)

DOE is a formal mathematical method for systematically planning and conducting scientific studies that change experimental variables together in order to determine their effect of a given response. It makes controlled changes to input variables in order to gain maximum amounts of information on cause and effect relationships with a minimum sample size. It generates information on the effect various factors have on a response variable and in some cases may be able to determine optimal settings for those factors. Application of Design of experiments leads to an understanding of the often complex relationship between the input parameters and the output. In the last half century, statisticians have devoted immense effort to the construction and study of layouts for experiments, with various criteria defined for improving the efficiency of designs [197,198].

Some of the important DOE methods are

- Taguchi
- Box Behnken
- Central composite circumscribed
- Central composite faced
- D-Optimal designs
- Response surface methods etc.

1.12.1 Taguchi method

Dr. Genichi Taguchi of Japan modified the classical DOE approach using 'orthogonal arrays' to improve the quality of a process / product. The various steps in the Taguchi method include:
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- Identification of main function, noise factors and objective function to be optimized
- Choice of control factors and their levels [199,200]
- Conduction of experiments based on orthogonal arrays
- Generation of factor effect plots and selection of optimum combination of control factors
- Conduction of a verification experiment and
- Recommendation of suitable parameter settings to produce acceptable products.

The Taguchi design is widely used in the polymer industry for optimizing polymerization conditions, tyre cord properties, composition of blends, injection molding parameters, etc. [201-203].

1.12.2 Orthogonal array

Orthogonal Arrays are special experimental designs that require only a small number of trials to discover main factors. It is nothing but a fractional factorial matrix, which assures balanced comparison of levels of any factor or interaction of factors. It is a matrix of numbers arranged in rows and columns. In orthogonal array, columns are mutually orthogonal. That is, for any pair of columns all combination of factor levels occurs and they occur at equal number of times. The number of columns of an orthogonal array represents the maximum number of factors that can be studied using that array. Among the various designs, the orthogonal array introduced by C. R. Rao in the forties [200] has been studied widely and is now recognized as a fundamental component in the statistical design of experiments. It has also been popularized, in particular, by its application in Taguchi methods [204,205].
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The orthogonal array specified by Taguchi has certain standard arrays. Some of the standard orthogonal arrays are:

\[ L_4(2^3) : \text{4 experiments, 2 levels and 3 columns} \]
\[ L_8(2^7) : \text{8 experiments, 2 levels and 7 columns} \]
\[ L_{18}(2^1*3^7) : \text{18 experiments, 3 levels and 8 columns} \]

A typical orthogonal array is shown in the Table 1.1

Table 1.1 Standard L4 orthogonal array

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Columns</th>
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<tbody>
<tr>
<td></td>
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</table>

1.13 SCOPE AND OBJECTIVES OF THE WORK

The evaluation of microwave properties of conducting polymers has not been exhaustive. Some studies have been done in polyaniline, polypyrrole and to a lesser extent on polythiophenes. So in this study the microwave properties of four important conducting polymers belonging to polyaniline polythiophene and polyazomethine families are proposed to be explored. Polyazomethines are particularly attractive because they show good mechanical strength, thermal stability, nonlinear optical properties, and photoconductivity. Polyanilines and polythiophenes have been extensively studied for a great number of applications.
and are used in many commercial fields. Design of experiments technique has been used in polycondensation reaction and this has helped to reduce the number of trials required to produce an optimum product with lowest cost.

One of the major drawbacks of conducting polymers is their poor processability, and this problem is proposed to be addressed in this investigation. Preparation of composites of conducting polymers has been found to improve the processibility. These composites can also improve the mechanical properties and physical characteristics. Conducting polymer/thermoplastic composites are proposed to be prepared by the in situ polymerization method to develop it as a semi IPN and hence reduce the phase separation.

The major objective of the study is to develop a processable thermoplastic conducting composite suitable for EMI shielding and microwave absorption. To achieve this, the electrical and microwave properties of conducting polymers like poly para phenylene diazomethine, polythiophene, polyaniline and that of poly (3, 4-ethylenedioxythiophene) (PEDOT) are proposed to be evaluated and compared. The polymers showing better microwave properties will be selected for further study. To improve the processability of these conducting polymers, their composites with thermoplastics are proposed to be developed. Microwave and electrical properties of these composites have to be evaluated and the most suitable composite will be selected for application studies. The most promising composite will be considered for EMI shielding and microwave absorption applications. An important objective of the work is the development of a processable conducting composite with very good electrical, mechanical and microwave properties which can be easily cast or coated on various surfaces.
The objectives of the study are summarized as

1. To optimize the polycondensation reaction conditions to prepare polyparaphenylene diazomethane (PPDA) using Taguchi Design of Experiments.

2. To synthesize polythiophene (PTH) and Poly(3,4-ethylenedioxythiophene) (PEDOT).

3. To characterize PPDA, PTH and PEDOT using FTIR, TGA and DSC.

4. To evaluate and compare the microwave properties like dielectric constant, dielectric loss, conductivity, absorption coefficient, heating coefficient, loss tangent and skin depth of PPDA, PTH, PEDOT and Polyaniline (PANI).

5. To optimize the ratio of FeCl₃ : Thiophene in preparing the insitu PTH-PVC composite.

6. To study the effect of drying condition on the microwave properties of PTH-PVC composite.

7. To prepare thermoplastic conducting polymer composites like PTH-PVC, PEDOT-PVC, PANI-PVC, PPDA-PVC, PANI-PU and PEDOT-PU.

8. To evaluate and compare the microwave properties of these thermoplastic conducting polymer composites for electrical and microwave applications. To select the most promising composite based on the electrical and microwave properties.
9. To study the EMI shielding and microwave absorption applications of the selected thermoplastic composite.

1.14 METHODOLOGY

The methodology proposed to be adopted to achieve the above objectives is detailed below.

**Step-I Synthesis and characterization of PPDA:**

A novel polyazomethine, PPDA, is proposed to be prepared by the condensation polymerization of para phenylene diamine and glyoxal trimeric dihydrate. The optimum reaction conditions will be determined by design of experiments. The prepared polymer has to be characterized by DSC, TGA and FTIR methods.

**Step-II Synthesis and characterization of polythiophene:**

Polythiophene is proposed to be prepared by chemical oxidative polymerization of thiophene with FeCl₃. The prepared polymer has to be characterized by DSC, TGA and FTIR methods.

**Step-III Synthesis and characterization of PEDOT:**

Poly (3, 4-ethylenedioxythiophene) is proposed to be prepared in DBSA micellar solution using FeCl₃ as the oxidant. This method has reported to give PEDOT nanoparticles with very high conductivity [206]. The prepared polymer will be characterized by DSC, TGA and FTIR methods.
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Step-IV Evaluation of microwave and electrical properties of the conducting polymers:

DC conductivity of the polymers is proposed to be evaluated using Keithley nanovoltmeter and microwave properties like dielectric constant, dielectric loss, conductivity, absorption coefficient, heating coefficient, loss tangent and skin depth of PPDA, PTH, PEDOT and Polyaniline (PANI) will be evaluated using cavity perturbation technique.

Step-V Optimization of the preparation conditions for PVC-PTH composites:

PVC-PTH composites will be prepared by polymerizing dispersed thiophene in PVC solution using chemical oxidative technique (in situ polymerization). The conditions for the preparation of PVC-PTH composite are to be optimized based on optimum microwave properties. The ratio of FeCl₃: Thiophene ratio for the in situ polymerization and the optimum casting conditions will be determined.

Step-VI Preparation of selected thermoplastic conducting composites:

Thermoplastic conducting composites like PTH-PVC, PEDOT-PVC, PANI-PVC, PPDA-PVC, PANI-PU and PEDOT-PU are proposed to be prepared by in situ polymerization technique as mentioned in Step V.
Step-VII Selection of the appropriate thermoplastic conducting composite for microwave applications:

The microwave and electrical properties of the various conducting composites will be evaluated and compared. The most suitable composite is to be selected for microwave and electrical application study.

Step-VIII EMI shielding and microwave absorption behavior of the selected composite:

Due to FeCl$_3$ content in the films, it was noted that the composites may absorb moisture on storage. To rectify this effect benzyl peroxide is proposed to be used as oxidant for the polymerization instead of FeCl$_3$. The EMI shielding and microwave absorption property of PU-PANI composite will be evaluated at S and X bands of microwave frequency and potential applications has to be discussed.
1.15 REFERENCES


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