Synthesis, Characterization & Measurement Techniques

As already mentioned in Chapter 1 (Section-1.6), the present work is focussed on a systematic study related to the electrical, optical and structural behaviour of PMMA-PAni blends. In this chapter, after a brief description of PMMA, the experimental procedure followed for the synthesis of different forms of Polyaniline (emeraldine salt) doped with Dodecyl benzene sulfonic acid (DBSA), Camphor sulfonic acid (CSA), Iron (Fe) and Copper (Cu), respectively has been discussed. Next, the method adopted for the preparation of PMMA-PAni blends on mixing the synthesized PANi in PMMA at various concentrations has been presented. Thereafter, various characterization techniques, like UV-Visible Spectroscopy (UV-VIS), Fourier Transform Infrared (FTIR) Spectroscopy and Raman Spectroscopy, used in the present study for characterizing PANi and PMMA-PANi blends, have been described. Finally, a brief description regarding the Current-Voltage (I-V) and dielectric measurements related to these blends is presented.

2.1 POLY(METHYL METHACRYLATE)

Poly(methyl methacrylate), generally named as PMMA and having the monomer composition \( \text{C}_5\text{H}_8\text{O}_2 \), is a linear, amorphous,
thermoplastic polymer with high transparency in almost entire visible range [Mark et al. 1985; Hong 2001; Leontyev 2001; Tatro et al. 2003; Hadjichristov et al. 2009; Lin 2010]. Due to this extraordinary feature, it is sometimes referred to as acrylic glass. The chemical structure of this polymer is as shown in figure 2.1 [Billmeyer 2005].

![Chemical structure of Poly(methyl methacrylate)](image)

**Figure 2.1: Chemical structure of Poly(methyl methacrylate)**

Some of the important physical parameters of PMMA [Wunderlich 1975; Billmeyer 1984; Stobl 1997; Brandrup et al. 1999; Mark 1999] are listed below:

- **Density** : 1.17-1.20 g/cm³
- **Optical Energy Gap** : 2.72 eV
- **Refractive index** : 1.49
- **Glass transition temperature (T₉)** : 105 °C
- **Melting point** : 160 °C
- **Working temperature Range** : -40 °C to +90 °C
- **Dielectric constant (at 1 MHz, 25⁰ C)** : 2.6
- **Dissipation Factor** : 0.04-0.06
- **Resistivity** : >10¹⁵ Ωcm
- **Thermal Conductivity** : 0.193 Wm⁻¹K⁻¹
- **Water absorption** : 0.3-0.4%

It is extraordinarily resistant to oxidative photodegradation [Hawkins 1972], remarkably stable to sunlight [Benfor and Tipper 1975] and displays good environmental stability [Billmeyer 1971]. Due
to such extraordinary features, in addition to its scientific and technological applications [Kuo 2003; Leontyev et al. 2003; Kulish 2003; Koval 2004; Sousa 2007; Dorranian 2009; Abdelrazek 2010; Fawzy 2011]; this polymer is widely being used in many day to day applications.

2.2 SYNTHESIS OF POLYANILINE

Different forms of Polyaniline (Emeraldine Salt) doped with Dodecyl benzene sulphonic acid (DBSA), Camphor sulphonic acid (CSA), Iron (Fe) and Copper (Cu) salts, have been synthesized chemically using oxidative polymerization method [Chen 2002]. The reactions were carried out at low temperature below 10 °C, to get PAni with high molecular weight [Macdiarmid et al. 1985; Arms and Miller 1988; Austrias et al. 1989; Cao et al. 1989; Genies et al. 1990; Kricheldorf 1992; Kang et al. 1995; Mav et al. 1999; Vijayan and trivedi 1999; Xie and Xiang 2000; Rao et al. 2001; Chen 2002; Negi and Adhyapak 2002]. The details of the procedure adopted are as follows:

2.2.1 Polyaniline Doped with DBSA (PAni.DBSA)

PAni.DBSA has been synthesized from aniline using DBSA as dopant and ammonium persulphate (APS) as oxidant. The molar ratio of aniline:DBSA:APS was kept as 1:1:1. First, the prepared milky white solution of aniline and DBSA (70 weight % in 2-propanol) in deionized water was stirred magnetically in ice-cooled environment and then, the precooled solution of APS was added to it dropwise, resulting in change in the colour of the solution from milky white to green. The so obtained viscous solution was kept at low temperature (below ~10 °C) for 24 hours. Subsequently, acetone was added to this solution to decrease its viscosity and favouring precipitation. This dispersion was filtered and the residue was washed repeatedly in deionized water till the filtrate became colourless. Then, the obtained powder was dried in vacuum oven at 70 °C for 48 hours. Finally, a dark green powder of PAni.DBSA was obtained.
2.2.2 Polyaniline Doped with CSA (PAni.CSA)

For the synthesis of PAni.CSA, the monomer (aniline), CSA as dopant and APS as oxidant were used in the molar ratio of 1:1:1. The cooled solution of APS in deionized water was added dropwise in the precooled transparent aqueous solution of aniline-CSA with continuous stirring. The obtained clear solution was kept at low temperature for 24 hours, resulting dark green suspension, which was filtered, repeatedly washed and dried in vacuum for 48 hours giving the dark green powder of PAni.CSA.

2.2.3 Polyaniline Doped with Fe Salt (PAni.Fe)

To synthesize PAni.Fe, the greenish brown solution of aniline and FeCl₃, prepared in deionized water, was allowed to cool in ice-cooled environment under stirring. The molarity ratio of aniline:FeCl₃:APS was kept as 1:1:1. Afterwards, the cooled APS solution in deionized water was put drop by drop in the above prepared solution of aniline-FeCl₃. After 24 hours of constant cooling followed by filtration, washing with deionized water and finally, on drying in vacuum oven for 48 hours, the dark green powder of PAni.Fe was obtained.

2.2.4 Polyaniline Doped with Cu Salt (PAni.Cu)

For the synthesis of PAni.Cu, aniline and CuCl₂ were dissolved in deionized water and a greenish coloured solution was obtained. The precooled solution of APS in deionized water was added in the prepared aniline-CuCl₂ solution dropwise and a dark bluish solution was resulted. The molarity ratio of aniline:CuCl₂:APS was kept as 1:1:1. After the 24 hours of cooling, this solution was turned to dark green suspension, which on filtration followed by washing with deionized water and drying in vacuum oven, resulted in a dark green powder of PAni.Cu.

In order to confirm the characteristics of prepared PAni powders having different dopants, the same were subjected to UV-Visible, FTIR and Raman spectroscopy. Their conduction and dielectric behaviour was analysed using V-I and dielectric measurements. Afterwards, to
make the blends of as prepared PAni with PMMA, the PAni salts were mixed with PMMA at different concentrations by weight following the procedure, as discussed in the next section.

2.3 PREPARATION OF PMMA-PANI BLENDS

The blends of PMMA with different weight % of PAni.DBSA, PAni.CSA, PAni.Fe and PAni.Cu were prepared through solution casting method by dissolving the as-prepared PAni (ES) powder at varying concentrations in PMMA taking Chloroform as solvent. The prepared blended solutions were put to glass petri-dishes, which after the evaporation of the solvent at room temperature, were converted to PMMA-PAni blends in the form of free standing films. In order to study the optical, electrical and dielectric response of the blends, these were subjected to UV-Visible spectroscopy, I-V measurements, and Dielectric spectroscopy, respectively. Further, the structural analysis of these blends was carried out through Fourier Transform Infrared (FTIR) and Raman spectroscopic techniques.

The following sections are devoted to the short details of various experimental and measurement techniques, as mentioned above, in order to reveal the induced changes in PMMA as an effect of blending with different weight % of synthesized PAni salts, as mentioned in Section-2.2.

2.4 UV-VISIBLE SPECTROSCOPY

Ultraviolet-Visible spectroscopy is one of the most important analytical techniques to characterize organic compounds, especially conjugated organic materials as these absorb energy in UV or Visible region [Pavia et al. 1994; Banwell and McCash 1995; Zerbi 1999]. This technique is most widely used due to its simplicity, versatility, speed, accuracy and cost-effectiveness.

2.4.1 Theory and Instrumentation

The absorption of electromagnetic radiations in the UV-Visible region generally involves the transition of an electron between the
electronic energy levels of the molecule [Campbell and White 1989; Kemp 1991; Pavia et al. 1994; Banwell and McCash 1995; Campbell et al. 2000; Gauglitz and Dinh 2003; Hollas 2005; Yadav 2007; Wilhelm 2008]. The energy supplied by the incident radiations will promote electrons from their ground state (bonding or non-bonding) orbitals to excited state (anti-bonding) orbitals. Figure 2.2 represents different kinds of electronic transitions involved in UV-Visible region, which are briefly discussed as follows [Campbell and White 1989; Pavia et al. 1994]:

![Diagram](image)

**Figure 2.2: Different electronic transitions in UV-Visible region**

**(a) σ to σ* Transitions**

These transitions are generally employed in the saturated hydrocarbons having only σ-bonds. In these transitions, an electron in a bonding s-orbital is excited to the corresponding anti-bonding orbital. The energy required for these transitions is quite large and generally does not appear in typical UV-Visible spectrum and falls in far ultraviolet region. For example, in case of methane, where only C–H bonds (σ-bonds) are present, the maximum absorption appears at about 150 nm.
(b) n to σ* Transitions

These transitions are favourable in saturated compounds containing atoms with lone pairs (non-bonding electrons). These occur at usually lesser energy than σ to σ* transitions. These can be initiated in wavelength range ~150 - 250 nm. The organic molecules having halogens, Nitrogen, Oxygen and Sulfur show absorption in this region.

(c) n to π* and π to π* Transitions

Mostly, the absorption spectroscopy of organic compounds is based on transitions of n or π electrons to the π* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the electromagnetic spectrum (~200-700 nm). These transitions need an unsaturated group in the molecule to provide the π electrons. The compounds containing double/triple bonds, or aromatic rings in their structure show these types of transitions.

The absorption of light in an organic molecule is generally due to the presence of unsaturated groups, such as C=C, C=O, −N=N−, −NO₂, or the benzene ring. A compound is more likely to absorb visible light when it contains a conjugated system of alternate C=C and C−C bonds, with the π -electrons delocalized over a larger area. Some of the compounds show two absorption bands. This is because the excitation of the π electron in the C=O leads to the π to π* transition and the excitation of one electron of the lone pair of electrons on the oxygen atom results in n to π* transition.

In case of an isolated atom, the UV-Visible absorption spectrum is expected to exhibit a single, discrete line corresponding to each transition while for the case of a molecule, the UV-Visible absorption usually occurs over a wide range of wavelengths because in a molecule, each electronic energy level (either in ground state or in excited state) is, generally, accompanied by a large number of vibrational and rotational energy levels, which are also quantized. Therefore, a molecule exhibits transitions in many states of rotational
and vibrational excitation. The energy levels for these states are quite closely spaced with energy difference smaller than those of electronic levels. Since the energy required to induce electronic transition is larger than the energy required to cause the vibrational and rotational transitions, the vibrational-rotational levels are superimposed on the electronic levels and a molecule may, therefore, undergo electronic and vibrational-rotational excitations simultaneously. The vibrational/rotational transitions are so closely spaced that the spectrometer cannot resolve them; rather, the instrument traces the envelope over the entire pattern. Thus, the combination of these transitions results in the broad band of absorption centered near the wavelength of major transition [Pavia et al. 1994].

Figure 2.3 presents a general layout [Campbell and White 1989] of a UV-Visible spectrophotometer. Typically, a UV-VIS spectrophotometer consists of a light source, a monochromator and a detector.

![Figure 2.3: General layout of UV-Visible spectrophotometer](image)

A single source covering the full UV-Visible wavelength range cannot be made available. Therefore, two independent sources, one for ultraviolet region (deuterium lamp) and other for visible region
(tungsten lamp) of electromagnetic spectrum are used. Incident electromagnetic radiation from the source passes through monochromator, consisting of a prism/diffraction grating, which makes the spectral components spread out followed by slit permitting only the desired wavelength to pass. Beam splitter splits the beam for sample and reference cells held in standard holders. Light passing through the sample is measured by a detector, commonly a photomultiplier tube (PMT), which records intensity of transmitted light, thus, providing the transmittance as a function of wavelength.

In the present work, we have used Shimadzu double beam double monochromator UV-Visible Spectrophotometer (UV-2550) equipped with integrating sphere assembly ISR-240A, covering the electromagnetic range from 190 nm to 900 nm to characterize the synthesized PAni salts. For PMMA and different PMMA-PAni (ES) films, PerkinElmer Lambda 750 UV/VIS/NIR Spectrometer was employed.

From the recorded spectra for pure PMMA and PMMA-PAni (ES) blends, the variation in optical energy gap with the change in the concentration of PAni in PMMA has been studied.

### 2.4.2 Determination of Optical Energy Gap ($E_{opt}$)

From the obtained UV-Visible spectrum for any compound, several optical parameters, e.g. refractive index, dispersion parameters, extinction coefficient and optical energy gap may be determined, which play a very imperative role in defining the optical properties of the system. Out of these parameters, optical energy gap is most extensively studied because it directly relates the optical response of the material with its electrical and luminescent behaviour.

The optical energy gap in polymers has been determined through optical absorption spectroscopy using the Tauc’s relation \cite{Tauc 1974; Das et al. 1999; Mathai et al. 2002; Sun et al. 2002; Raja et al. 2003; Biederman 2004; Migahed and Zidan 2006}

\[
(\alpha h\nu) = B(h\nu - E_{opt})^Y
\]
where, $\alpha$ is the absorption coefficient corresponding to the fundamental absorption edge in UV-Visible spectrum, $hv$ is the energy of photon, $\gamma$ is a parameter connected with the distribution of density of states (DOS) in the transport gap (in the band tails) and $B$ is a proportionality factor that also provides information about the DOS distribution. It is connected with the length of tails of the localized states. Smaller values of $B$ indicate longer tails of these states. The value of $\gamma$ [Fink 2004] can be taken to be 1/2 for allowed direct transitions, 1 for transitions between density of states at band edges, 3/2 for forbidden direct transitions, 2 for indirect transitions with phonons and 3 for transitions between valance and conduction band-edge tails.

2.5 FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

Infrared (IR) Spectroscopy is a powerful tool for identifying the types of chemical bonds in a molecule by recording its infrared absorption spectrum. It is one of the most powerful spectroscopic tools available for the analysis of polymeric systems [Kemp 1991; Pavia et al. 1994; Banwell and McCash 1995; Koenig 1999; Zerbi 1999; Campbell et al. 2000; Coates 2000; Chalmers and Griffiths 2002; Gauglitz and Dinh 2003; Hollas 2005; Smith and Dent 2005; Wilhelm 2008]. IR spectroscopy is molecular specific with high sensitivity. It is based on the absorption or attenuation of electromagnetic radiation by specified motion of chemical bonds present in a molecule.

Theory and Instrumentation

When infrared radiations pass through the material, these are absorbed only at frequencies corresponding to the molecular modes of vibrations and a plot of transmitted radiation intensity versus frequency shows absorption bands. Infrared spectroscopy measures the vibrational energy levels of molecules. As the vibrational energy levels are distinctive for each molecule (and its isomers), the
vibrational spectrum has often been called the fingerprint of a molecule [Pavia et al. 1994; Koenig 1999].

In the IR absorption process, not all bonds in a molecule, but only those that have a dipole moment which changes as a function of time, can absorb infrared energy. This changing electrical dipole moment on interaction with the field of the incoming IR radiation is responsible for absorption. Symmetric bonds, such as those of N₂, O₂ or Cl₂, do not absorb infrared radiations because they do not have permanent dipole moment [Pavia et al. 1994; Koenig 1999; Kumar 2008].

The earlier infrared spectrometers were of the dispersive type. These instruments separated the individual frequencies emitted from the infrared source by using an infrared prism or grating. The detector measured the intensity at each frequency, which had passed through the sample and resulted in a plot of intensity versus frequency. But slow scanning process and low signal-to-noise ratio were the major limitations of the dispersive type IR-spectrometer.

Fourier Transform Infrared Spectrometer provides the simultaneous measurements of all the infrared frequencies, rather than individual ones. Figure 2.4 presents a basic layout of this spectrometer. It makes use of the Michelson interferometer [Campbell and White 1989; Silverstein et al. 1991], which has two mutually perpendicular mirrors one of which remains stationary while the other is movable. A beam splitter, constructed from an IR-transparent material, divides the incoming IR beam into two beams of equal intensity traversing towards the two mirrors of the interferometer. These beams reflect off from the respective mirrors and recombine when they meet back at the beam-splitter. With the continuous motion of one mirror, the path length of one beam remains fixed while that of other is constantly changing. The output signal of the interferometer is the result of interference of these two beams. The resulting signal is called an interferogram, which has the unique property that every data point, making up the signal, has information about every infrared frequency coming from the source. This interferogram is allowed to
pass through the sample and the detector records the transmitted signal with attenuated intensities.

As the data analysis requires a frequency spectrum (a plot of the intensity at each individual frequency) for identification, therefore, the measured interferogram signal, which is a time domain signal, cannot be interpreted directly. Therefore, a method of decoding the individual frequencies is required, which can be accomplished via a well-known mathematical technique, called the Fourier transformation. With the use of this method, the desired spectral information for analysis can be obtained. From the analysis of the spectrum received from FTIR, the presence of various bonds and their number can be estimated.

**Figure 2.4: Schematic layout of FTIR spectrometer**

Fourier transform infrared spectroscopy has some unique features [Koenig 1999] like

- It is a non-destructive technique.
- It provides precise measurements and requires no external calibration.
- It has high speed as it simultaneously records the full spectrum in less than a second.
- Spectral resolution can be adjusted according to the requirement.
- It has high signal-to-noise ratio as a large number of scans can be averaged.
- It is mechanically simple with only one moving part.
- It provides accurate wavelengths based on internal laser calibration.

In the present work, PerkinElmer ABB FTIR has been used to deduce the structural information of PMMA and the induced structural changes on blending it with different salts of PANi.

### 2.6 RAMAN SPECTROSCOPY

Like Infrared (IR), Raman spectroscopy is also used to reveal the molecular structure and composition of inorganic and organic materials [Sibilia 1988; Banwell and McCash 1995; Campbell et al. 2000; Koenig 2001; Chalmers and Griffiths 2002; Smith and Dent 2005]. However, the method of operation of these spectroscopic techniques is different. In IR spectroscopy, infrared radiation covering a range of frequencies is directed onto the sample. Absorption occurs where the frequency of the incident radiation is compatible to that corresponding to vibrational excited state of the molecule. Conversely, in Raman spectroscopy, the radiation from a monochromatic source (generally a laser) is allowed to scatter from the molecule. In this spectroscopy, it is the change in frequency, rather than the incident frequency itself, which provides the information of the vibrational states of the molecule. In Raman scattering, the irradiated light interacts with the molecule and distorts (polarizes) the cloud of electrons around the nuclei to form short-lived virtual states. The transitions between these virtual states and the normal states of the molecule cause the Raman scattering [Smith and Dent 2005].
Further, intense Raman scattering occurs from vibrations, which cause a change in the polarizability of the electron cloud round the molecule. Usually, this polarization is dominant in symmetric molecules and thus, results in the maximum changes. This is in contrast with infrared absorption where the most intense absorption is caused by a largest change in dipole moment, which is caused by asymmetric vibrations. Thus, the presence of a permanent dipole moment, which is must for IR absorption, is not required for Raman spectroscopy. Therefore, not all vibrations of a molecule need to be both infrared and Raman active, and the two techniques usually give quite different intensity patterns. As a result, the two are often assumed complementary and used together to have a better view of the vibrational structure of a molecule [Smith and Dent 2005].

Theory and Instrumentation

The Raman scattering occurs when a material is irradiated by monochromatic light, causing a small fraction of the scattered radiation to exhibit shifted frequencies that correspond to the vibrational transitions of the molecule. Figure 2.5 shows the possible vibrational transitions, which occur for a single vibration [Sibilia 1988; Banwell and McCash 1995; Campbell et al. 2000; Smith and Dent 2005].

At room temperature, most of the molecules, but not all, are present in the lowest energy vibrational level. Since the virtual states are not real states of the molecule and are created when the incident monochromatic radiation interacts with the electrons and causes polarization and thus, the energy of these states is dependent on the frequency of the light source used. The Rayleigh transitions are the most intense transitions since most photons scatter this way. These do not involve any energy change and consequently, the light returns to the same energy state. The Raman scattering process from the ground vibrational state \( E_{\text{ground}} \) leads to absorption of energy by the molecule and its promotion to a higher energy excited vibrational state \( E_{\text{excited}} \) by means of interaction with the irradiated monochromatic light. This is called Stokes scattering. However, due to thermal energy, there
may be some molecules present in an excited state ($E_{\text{excited}}$) and scattering from these states to the ground state ($E_{\text{ground}}$) is called **anti-Stokes scattering** and involves transfer of energy to the scattered photon.

More precisely, *ground-state molecules produce lines shifted to energies lower than the source energy, while the slightly weaker lines at higher frequency are due to molecules in excited vibrational states. These lines as a result of the inelastic scattering of light by the sample are called Stokes and anti-Stokes lines, respectively. Elastic collisions resulting in Rayleigh scattering produce much more intense lines at the same frequency as that of the incident light.*

![Figure 2.5: Raman scattering between different vibrational levels](image)

The essential components of Raman spectrometer [*Campbell and White 1989*] are shown in figure 2.6. The configuration for a Raman dispersive experiment basically consists of five parts: laser, sample, dispersing element, detector and computer. A monochromatic laser beam (excitation radiation) is focused on the scattering sample. The scattered light from the sample is focused on the entrance slit of the monochromator and dispersed. The dispersion element discriminates between the strong elastic scattering (Rayleigh scattering) and the weak inelastically scattered light (Raman scattering) with different
frequencies. The Raman spectrum is recorded by the detection of the intensity of the scattered, frequency-shifted light by a photo-detector. The resulting signal of the detector is amplified and converted to a form appropriate for plotting as a function of frequency or wavenumber. Different peaks in the spectrum correspond to different bonds present in the molecule.

![Schematic representation of Raman spectrometer](image)

**Figure 2.6: Schematic representation of Raman spectrometer**

Raman spectroscopy [Smith and Dent 2005] has a number of advantages, which enforce the use of this method as structural informer:

- Raman spectroscopy is a scattering process and therefore, samples of any size or shape can be examined.
- Glass and closed containers can be used for sampling.
- Fiber optics can be used for remote sampling.
- Aqueous solutions can be analyzed easily as water is weak Raman scatterer.
- A single instrument can be used to scan the region from 10-4000 cm\(^{-1}\).
Small samples can be studied since the laser beam can be focused down to about a spot with a diameter of 100 µm.

In the present study, the Jobin-Yvon HR-800 Raman spectrometer (He-Ne laser, λ = 632.8 nm), available at UGC-DAE-CSR, Indore have been used to record the Raman spectra of pure PMMA, PANi (ES forms) and their blends, synthesized as discussed in Section-2.2.

2.7 ELECTRICAL MEASUREMENTS

2.7.1 DC Conductivity

Conductivity of a specimen depends upon the factors like, the number of charge carriers, nature of charge species and temperature. Various methods, such as two probe, four probe, Van-der Pauw and circular ring electrode, etc. [Sze 2004] are used to determine the conductivity of a material. The method used to determine the conductivity, generally depends upon the nature of the material [Blythe 1984].

- Low-resistivity materials, for which the contact resistance being of major importance, require four-terminal method for reliable measurements.
- For high-resistivity materials, contact resistance is of only minor significance and leakage current, especially over surfaces, becomes the more serious problem. For this reason, three-terminal method, using a guard electrode, is commonly used to nullify the problem.

Circular Guard Ring Electrode Method

This method is of great importance for highly resistive materials, e.g. polymeric materials. As the conductivity of these materials is very small, hence, the main problem becomes the leakage current from the high-voltage source to the ammeter via routes other than the intended one through the specimen. The surface of the specimen provides a low resistance path due to the accumulation of dirt and moisture on it. For this reason, a third terminal, i.e. the extra guard ring electrode, is introduced around the low-voltage electrode and is connected to the
ammeter so as to intercept and divert any leakage currents, which are excluded from the ammeter reading. The schematic diagram for the resistivity measurement using three electrode method is shown in figure 2.7 [Blythe 1979, 1984; Blythe and Bloor 2005].

![Schematic diagram for the resistivity measurement using three electrode method](image)

**Figure 2.7: Schematic representation of guard ring electrode method**

Bulk resistivity is measured by applying a voltage across opposite sides of the insulator specimen. From the measured values of the resultant current through the specimen, the bulk resistivity ($\rho$) is determined using the expression

$$\rho = \frac{K_v R}{t}$$

where, $K_v$ is the effective area of the guarded electrode, $t$ is average thickness of the sample and $R$ is resistance of the sample determined through $V$-$I$ measurements.

If the electrodes used are circular in dimensions, then

$$K_v = \pi \left( \frac{D_1}{2} + B \frac{g}{2} \right)^2$$
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with \(D_1\) as the outside diameter of guarded electrode, \(g\) is the distance between the guarded electrode and the ring electrode and \(B\) is the effective area coefficient.

Bulk dc conductivity \((\sigma_{dc})\) of any specimen can be found by taking the reciprocal of the resistivity, calculated using above expression, and can be represented as

\[
\sigma_{dc} = \frac{1}{\rho}
\]

In the present work, conductivity of PMMA and various PMMA-PAni(ES) blends has been determined using the Keithley 6517A electrometer attached with Model 8009 resistivity text fixture having interface with computer.

For the present set-up, the value of \(K_v\) is provided to be 22.9 for \(R\) to be measured in ohm and \(t\) in cm. Accordingly, the resistivity of the sample is given by

\[
\rho (\text{in } S/cm) = \frac{22.9}{t \text{ (in cm)}} R
\]

Thickness \((t)\) of the samples has been measured using digital screw guage, having least count 1 \(\mu\)m, and resistance \((R)\) has been estimated from the plotted V-I curves.

2.7.2 Dielectric Studies

Dielectric measurements include the study of dielectric constant, dielectric loss, relaxation time, electric modulus, ac conductivity, etc. This measurement technique is sensitive to dipolar species as well as localized charges in the material [Boyd and Smith 2007; Te-Nijenhuis 2009]. As explained in Chapter 1, Section-1.5 that whenever a dielectric is placed in an alternating electric field, depending on the frequency of the field, it may polarize through different mechanisms [Raju 2003; Kao 2004; Blythe and Bloor 2005; Boyd and Smith 2007]. As a result, polarization vector \(\vec{P}\) (a measure of polarization in the
material) and displacement vector (\( \vec{D} \)) lag behind the electric field vector (\( \vec{E} \)) in phase and a loss of energy takes place, which is responsible for the complex nature of the dielectric constant [Mardare and Rusu 2004; Bhargav et al. 2008]. The loss factor (\( \tan \delta \)) is the primary criterion for the usefulness of a dielectric as insulator. To attain the high capacitance in the smallest physical space, materials with high dielectric constant and low loss factor are required. The imaginary part of complex dielectric constant gives the dielectric loss.

To study the frequency dependent dielectric properties of PMMA and PMMA-PAni blends, the dielectric measurements were carried out in the frequency range from 20 Hz to 5 MHz using Aligent 4285A Precision LCR meter. The values of capacitance (\( C \)) and tangent loss (\( \tan \delta \)) of the polymeric dielectric material were recorded from the instrument. From these values, the real part of dielectric constant (\( \varepsilon' \)) (component of energy stored in each cycle of the electric field) and imaginary part of the dielectric constant (\( \varepsilon'' \)) (component of energy dissipated in each cycle of the electric field) were calculated using the following relations [Kao 2004; Blythe and Bloor 2005]

\[
\varepsilon' = \frac{Cd}{\varepsilon_0 A}
\]
\[
\varepsilon'' = \varepsilon' \tan \delta
\]

where, \( d \) is the thickness of the sample, \( A \) is the area of the electrode and \( \varepsilon_0 (= 8.854 \times 10^{-12} \text{ F/m}) \) is the permittivity of the free space.

Another important parameter, which measures the rate of movement of charge species present in the dielectric when an alternating field is applied, is ac conductivity (\( \sigma_{ac} \)). It is related to the dielectric loss and frequency as [Kao 2004; Blythe and Bloor 2005]

\[
\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon''
\]

From these calculated frequency dependent parameters, the complete dielectric behaviour of PMMA and its blends with various emeraldine salt form of PAni have been estimated.
The experimental results related to the optical, electrical and structural behaviour of PMMA-PAni blends and their interpretation are presented in the subsequent chapters.
REFERENCES


Kuo S.W., Kao H.C., Chang F.C., “Thermal behavior and specific interaction in high glass transition temperature PMMA copolymer”, Polymer 44 (2003) 6873.


