Chapter 4

Theoretical Consideration
4.1 Theory of X-Ray Diffraction and Infrared Spectroscopy:

4.1.1 Theory of X-Ray Diffraction:

X-ray diffraction is one of the most widely used instrumental techniques in the various branches of material science. The systematic studies of the X-ray powder diffraction began in Germany by Debye and Scherrer (1916). Generally the percentage crystallinity in the sample (thin film, glass etc) can be determined from the intensity versus \(2\theta\) curve. The powder photographic method can be used from which ‘d’ values are calculated. X-ray diffraction is used to identify the second phase and decide the conditions, of its occurrence (Dixit 1982). Diffraction pattern of an amorphous solid consists of broad haloes or rings, which vanish rapidly with increasing glancing angle and the sharp rings would indicate some degree of crystallinity. The approximate estimation of percentage crystallinity of the samples can be done as per the relation suggested by Kaelble (1967).

\[
\text{Percentage crystallinity} = \frac{I_c \times 100}{I_c + kI_A} \tag{4.1}
\]

where,

\[I_c = \text{Area of crystalline fraction}\]
\[I_A = \text{Area of amorphous fraction}\]
\[k = \text{constant equal to unity}\]
4.1.2 Theory of IR Spectra:

Infrared spectroscopy is used to know the existence of different bonds and bond transformation if any. Mid infrared absorption spectroscopy will be used to know the existence of different bonds and bond transformation, if any.

The atoms of chemical substance are in a state of continuous vibration of slightly different frequencies. When IR radiation is incident on a sample resonant absorption takes place and closed packed absorption bands appear. These are called as IR absorption spectra. Emission or absorption spectra arise when molecules undergo transitions between quantum states corresponding to two different internal energies. The energy difference $\Delta E$ between the states is related to the frequency of radiation emitted or absorbed by the quantum relation $\Delta E = h\nu$.

There are four ranges of IR radiation (Gurudeep and Chatwal 1984).

1) The photographic region-visible to 1.2$\mu$
2) The very near infrared region-form 1.2$\mu$ to 2.5$\mu$
3) The near infrared region- from 2.5$\mu$ to 25$\mu$, know as vibration rotation region
4) The far infrared region-from 25$\mu$ to 300-400$\mu$ is known as the rotation region.

For absorption of infrared radiation, correct wavelength of radiation and electric dipoles are required. To understand the theory of IR absorption spectroscopy, knowledge of vibrational-rotational spectra is necessary. This is very well known and therefore it is not given (Burghate 1997).
The frequency of vibration \( (v) \) is given by,

\[
v = \frac{\omega}{2} = \left( \frac{1}{2\pi} \right) \left( \frac{k}{\mu} \right)^{1/2}
\]

where,

\( k \) - is the force of constant in dyes/cm
\( \mu \) - is the reduced mass of the system

The frequencies of the centres of fundamental, first and second overtones are given by,

i) for fundamental band
\[
v = (1 - 2x) \pi_o
\]

ii) for first overtone band
\[
v = (1 - 3x) \pi_o
\]

ii) for second overtone band
\[
v = (1 - 4x) \pi_o
\]

where,

\( x \) = anharmonic constant

\( \pi_o \) = equilibrium frequency of the molecule expressed in wave number

4.2 Theory of Electrical Conductivity:

The electrical conductivity \( (\sigma) \) in polymers varies exponentially with temperature and electric field \( E \) (Seanor 1982) as

\[
\sigma = \sigma_o \exp (-E_a/kT)
\]

where,

\( E_a \) is activation energy of conduction. The changes in \( E_a \) are found in the
neighborhood of the glass transition temperature ($T_g$). The activation energy $E_a$ can be determined from $(\ln \sigma V_s 1000/T)$ Arrhenius plots.

**Charge Carriers**

The electrical conductivity of polymers increases with temperature. The non-ohmic behaviours is due is ionic conduction. The mass transport measurements have shown that the non-linear current voltage characteristics arise due to ionic conduction. The charge carriers in polymers can arise from

i) Intrinsic charge carrier generation.

ii) Impurity conduction.

iii) Injection processes by the electrode.

**Intrinsic Charge-Carrier Generation (Due to Thermal Processes)**

The materials are classified on the basis of their electrical properties as follows,

a) Metals, in which resistivity increases with temperature.

b) Semiconductor or insulators in which resistivity decreases with temperature but in semiconductor the decrease in resistivity is much larger than that in insulators.

In solids there is the highest filled band called valance band, the lowest empty band called the conduction band. The difference in energy between them is called the forbidden energy gap. The conducting properties of solids are controlled by the width of forbidden energy band and the range of allowed energies in the conduction and valence bands. In a strongly interacting system the allowed bands are wide and
in a weakly interacting system, such as molecular crystal, the bands are narrow. Within the band the energy levels remain discrete but are closely spaced.

Effective mass of charge is related to the width of the energy band. In a narrow band, the effective mass is high and the mobility low and the charge carriers respond slowly to the applied electric field. In polymers, it has been calculated that the bandwidth for a single linear polymethylene chain should be large (McCubbin and Manne 1968). However, due to the disorder and relatively large distances between polymer chain, there will be a transfer of charge carriers between adjacent polymer segment or between specific sites which may be on the same or on a different polymer chain. Intrinsic conduction in semiconductor arises by excitation of electron across the forbidden energy gap.

**Extrinsic Charge Carrier Generation (Doping with External Impurities)**

If an electron donor or an electron acceptor impurities are introduced into the host matrix, the electrical properties can be controlled in a way similar to that in which doping of inorganic crystals by altervalent ions is used to create n or p type conduction.

Another way to increase conductivity is to produce materials that are mixtures of easily ionizable electron donors and electron acceptors. Those materials in which the charge is shared between donor and the acceptor are called the charge transfer complexes. A number of these compounds have been shown to be conductive. The conductivity depends upon the ionic character of the complex. Fully ionic compounds are more conductive in the ground state than weakly ionic compounds (Williams 1976).
Localized State

In many polymers there are polar groups. Each dipole can act as an electron or hole trap. The bulk structure of the polymer is dependent upon factors such as the chemistry of monomers and the stereochemistry of the polymer.

Many polymers are semicrystalline. The increase in crystallinity reduces conductivity. If the conduction is ionic, ion mobility through the crystalline region will be low, if it is electronic, it will perhaps be faster, but the crystalline amorphous boundary acts as a trapping region.

Wholly amorphous polymers exist in two states depending upon their temperature. At low temperature they are hard, glassy materials. Above the glass transition temperature \( T_g \) they undergo transition to a rubber-like state. The change in conductivity occurs due to the onset of the molecular motion above \( T_g \).

The transition between glassy and amorphous states is accompanied by the “freeing up” of gross molecular motions of the polymer chain. Other types of transition have also been identified with the onset of other molecular motion (Mc Crum et al 1967) in amorphous material. They occur in the order of increasing temperature.

(a) Side-chain motion (rotations).
(b) Motion of two, four-carbon moieties in the main chain (Schatzki-Cranshaft effect).
(c) Motion of moieties containing heteroatoms in the polymer chains.
(d) Motion of the segments containing 50-100 backbone atoms
   (corresponding to \( T_g \)).
(e) Motion of the entire chain as unit.

In crystalline polymers, additional possibilities exist, like

a) Crystal melting
b) Change in crystalline structure
c) Motion of side change in crystallite
d) Crystalline-amorphous interactions
e) Intercrystalline interactions.

Escape from these localized states may be purely thermal, it may depend on the local environment and the specific molecular motion.

The localized states may act as trapping centers from the extended states of crystalline region. In the language of semiconductor theory, a neutral acceptor state, or an ionized donor state will trap electrons, and a neutral donor state or an ionized acceptor state will trap hole. A trapped charge can also act as recombination centre.

**Injection Processes**

The generation of charge carriers can also occur due to the emission from electrode or generation under the influence of light (photo conduction), direct emission from electrodes in particularly important at high fields.

At higher fields the influence of electrode processes on the apparent electrical properties is very important. Electrons in a metal (electrode) are free to move through out its bulk. However, when they reach the surface and if they find dielectric instead of vacuum they require excess energy to enter the dielectric. This modifies the potential barrier of the metal. In such case both electrons and
holes can be injected depending upon the energy levels in the dielectric. Such processes can be represented by the equation,

\[ M^+ + P \rightarrow M + P^+ \text{ at the anode} \]
\[ M^+ + P \rightarrow M + P^+ \text{ at the cathode} \]

where, M-metal and P-polymer.

The surface of the polymer is complex. The surface states extend some distance into the polymer. On making the contact between the electrode and the polymer, electron transfer will take place until thermodynamic equilibrium is attained. The contact charge will cause some loosening of barrier to injection. There are three methods in which the energy required to escape from the metal may be obtained, as

i) By thermal methods (thermionic emission)

ii) By application of high electric field and

iii) By photon absorption at sufficient short wave lengths in the photoemission process.

Mechanism i) and iii) may be modified by the Schottky effect which arises from the field dependent lowering of the potential barrier.

**Poole-Frenkel Mechanism**

The current-voltage relationship for Poole-Frenkel mechanism is (Frenkel et al 1928) expressed as

\[ J = B \exp \left[ \frac{-\Phi}{kT} + \beta PF \frac{E}{2} \right] \]

(4.4)

where, B = constant
\[ \beta_{pf} = \frac{e}{kT} \left( \frac{e}{\pi \varepsilon \varepsilon_0 d} \right)^{1/2} = \text{constant} \]  \hspace{1cm} (4.5)

where, \( \varphi \) - potential barrier

\( e \) - electronic charge

\( k \) - Boltzman’s constant

\( T \) - temperature in Kelvin

\( \varepsilon_0 \) - permitivity of free space

\( \varepsilon \) - dielectric constant

\( d \) - thickness of sample

The Poole-Frenkel mechanism predicts a field dependent conductivity expressed as

\[ \sigma = \sigma_0 \exp \left( \frac{\beta_{pf} E^{1/2}}{2kT} \right) \]  \hspace{1cm} (4.6)

or

\[ \ln \sigma = \ln \sigma_0 + \left( \frac{\beta_{pf} E^{1/2}}{2kT} \right) \]  \hspace{1cm} (4.7)

Poole-Frenkel mechanism demands a linear relation between \( \ln \sigma \) and \( \sqrt{E} \) with +ve slope.

**Fowler-Nordheim mechanism**

The Fowler-Nordheim relation (Fowler et al 1928) for current density is

\[ J = AV^2 \exp \left( -\frac{\varphi}{V} \right) \]  \hspace{1cm} (4.8)

or

\[ \ln \left( \frac{J}{V^2} \right) = \ln A - \left( \frac{\varphi}{V} \right) \]  \hspace{1cm} (4.9)

and \( \ln (J/V^2) \) versus \( 1000/V \) plots is expected to be a straight line with a -ve slope.
**Schottky Mechanism**

The Schottky-Richardson current voltage relationship is expressed as

\[
J = AT^2 \exp \left[ -\frac{\Phi_s}{kT} + \beta_{SR} E^{1/2} \right] 
\]  
(4.10)

\[
\beta_{SR} = \frac{e}{kT} \left[ \frac{e}{4\pi\varepsilon_0 d} \right]^{1/2} 
\]  
(4.11)

where,

\( A \) - constant

\( \Phi_s \) - metal insulator potential barrier

\( \beta_{SR} \) - Schottky field lowering constant, and hence

\[
\ln J = \ln AT^2 - \frac{\Phi_s}{kT} + \beta_{SR} E^{1/2} 
\]  
(4.12)

i.e. \( \ln J \sqrt{E} \) plots should be a straight line with a +ve slope.

**Richardson Mechanism**

The Richardson current voltage relationship is expressed as,

\[
\frac{J}{T^2} = A \exp \left[ -\frac{\Phi_s}{kT} + \beta_{SR} E^{1/2} \right] 
\]  
(4.13)

\[
\ln \frac{J}{T^2} = \ln A + \left[ -\frac{\Phi_s}{kT} + \beta_{SR} E^{1/2} \right] 
\]  
(4.14)

\[
\ln \frac{J}{T^2} = \ln A + \beta_{SR} E^{1/2} - \frac{\Phi_s}{kT} 
\]  
(4.15)

The graph between \( \ln (J/T^2) \) \( \sqrt{E} \) from this relation should be a straight line with a -ve slope.
4.3  Theory of Thermally Stimulated Discharge Current:  
Charging and Polarizing Methods

Methods for forming space-charge electrets and dipolar electrets differ frequently. The charging of space-charge (or surface-charge) electrets is mostly achieved by injecting (or deposition) charge carriers by discharges, particle beam, contact electrification or other techniques through a non-metallized surface. Injection from a deposited metal layer is also possible at relatively high fields. Other methods consist in the generation of carriers within the dielectric by light, radiation or heat and simultaneously charge separation by a field (Sessler 1980).

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Fig. (a): Schematic cross section of a one-sided metallized electret having deposited surface charges, injected space charges, aligned dipolar charges and compensation charges.

Fig. (b): Schematic cross-section of two-sided metallized electret with dipolar and space charges.
Thermal Charging Methods

Thermal methods of electret charging or polarization consist in the application of an electric field to a dielectric at an elevated temperature and subsequent cooling while the field is still applied. For polymers a elevated temperature is above the glass transition temperature but well below the melting point is selected. Electrets formed by thermal methods are referred to as thermo-electrets.

Three kinds of phenomena can occur in thermal charging namely

i) Internal polarization with the sign of a heterocharge due to dipole alignment or charge separation within the dielectric (dielectric absorption).

ii) Homocharge deposition due to spark discharges in the air gaps, and

iii) Homocharge injection through contacting electrodes.

The relative importance of these phenomena depend among others,

a) On the geometry of the experiment

b) On temperature and field strength prevailing during the charging process and

c) On the physics of the electrode-dielectric interface.

Dipole alignment occurs at elevated temperatures where the molecules or molecular chains are sufficiently mobile. While cooling, the aligned dipoles are frozen in, giving the dielectric a permanent polarization. The alignment is controlled by the Debye equation relating the change in polarization to the already existing polarization $P_p$, the electric field $E$ and the distribution of
dipole-relaxation frequencies. Assuming first a single dipole-relaxation frequency $\alpha(T)$ (Turnhout, 1975).

$$\frac{dP_p(t)}{dt} + \alpha(T) P_p(t) = \varepsilon_s (\varepsilon_s - \varepsilon_o) \alpha(T) E$$

(4.16)

here $\varepsilon_s$ and $\varepsilon_o$ are the (weakly temperature dependent) static and optical dielectric constants respectively.

If the dielectric is cooled during a time period sufficiently short compared to the time it is kept at the forming temperature, the dipoles align predominantly during the elevated temperature phase and an isothermal solution of (4.16) is reasonably accurate. In this case, setting $P_p(0) = 0$, the time dependence of the polarization follows as,

$$P_p(t) = \varepsilon_o (\varepsilon_s - \varepsilon_o) E \left[ 1 - e^{-\alpha(T)t} \right]$$

(4.17)

which yields a maximum value of $\varepsilon_o (\varepsilon_s - \varepsilon_o) E$ for $P_p(t)$ at $t = 0$.

$P_p(0) = E \varepsilon_o (\varepsilon_s - \varepsilon_o)$

For polymers the temperature dependence of a dipole relaxation frequency below the glass transition point is generally given by,

$$\alpha(T) = \alpha_o \exp \left( -\frac{E_a}{kT} \right)$$

(4.18)

where,

$\alpha_o$ is the natural relaxation frequency,

$E_a$ is a dipolar activation energy.

A formally similar relation ship (with $T$ replaced by $T - T_\infty$) holds at higher temperature. Thus for small $t$, the polarization with a single $\alpha(T)$ increases as

$$P_p(t) = \varepsilon_o (\varepsilon_s - \varepsilon_o) E \alpha_o t \exp \left( -\frac{E_a}{kT} \right)$$

(4.19)

The polarization buildup is therefore weakly field dependent and strongly
temperature dependent in the sense that it is favored by higher temperatures. For a distribution of relaxation frequencies, which may be due to a distribution of activation energies $E_a$ or a distribution of pre-exponential factor $\alpha_o$, this dependence of $P_p$ on field and temperature is essentially preserved.

**Evaluation of TSD Current Data**

By the TSDC technique the thermally activated release of stored dielectric polarization is studied. The various parameters of a polarized sample can be found by a single set of measurements, *viz.* the thermally stimulated discharge current (TSDC). In thermograms the peaks occur because the release of charge is faster over a certain range of temperature. The temperature at which peak occurs depends on activation energy of the corresponding trapping centre in the sample.

The polarization in a dielectric is caused by

i) Orientation of dipoles.

ii) Transference of space charge.

iii) Injected surface charge from electrodes.

If the sample is polarized at a temperature $T_p$, the polarization will acquire an equilibrium value. According to Bucci et al (1966), the depolarization current at any time ‘t’ due to dipolar reorientation on heating a polarized dielectric specimen is given by,

$$i(t) = A \exp \left[ \frac{-E_a}{kT} - \frac{1}{\beta \tau_o} \int \exp \left( \frac{-E_a}{kT} \right) dt \right]$$  \hspace{1cm} (4.20)

where, $A$ is constant,
k is the Boltzman’s constant 

$E_a$ is the activation energy 

$T_o$ is the room temperature 

T is the temperature attained by the specimen in time ‘t’.

β is the uniform heating rate 

$\tau_o$ is the characteristics relaxation time given by the expression

$$\tau = \tau_o \exp \left( \frac{E_a}{kT} \right) \quad (4.21)$$

where $\tau$ is the relaxation time of dipoles at the temperature $T$. The relation represented by Eq. (4.21) shows a peak at $T_m$, which has the following relation with $\tau_o$ (Khare and Srivastava 1992).

$$\tau_o = \left[ \frac{kT_m^2}{\beta E_a \exp \left( \frac{E_a}{kT_m} \right)} \right] \quad (4.22)$$

The values of $E_a$ can be determined from the low temperature tail of Eq. 4.20 using.

$$\ln i(t) = \ln A - \frac{E_a}{kT} \quad (4.23)$$

The equation 4.23 can be obtained by differentiating Eq. 4.20 and equating $di/dt$ to zero after substituting the value of constant A (Khare and Srivastava, 1992). Thus a plot $\ln I$ versus 1000/T gives a straight line both slopes gives the value of $E_a$. This is called the initial rise method of Garlick and Gibson.
4.4 Theory of Optical Properties:

The general theory of optical absorption by amorphous semiconductors has been outlined by Mott and Davis (1979). Mott (1967) shows that there are some similarities between the energy band structure of crystalline and glassy non-metallic materials. The crystalline materials show well-defined energy bands with sharp conduction and valence band edges. The glassy materials show band-tailing into the normally forbidden gap (Rashed and Ghani 1984).

The form of the energy dependence of the optical absorption typically observed is shown in the figure (4.1.1) (Elliott, 1984). The section is divided into two parts, with optical transitions at energies above and below the mobility gap. The difference between the energies of the mobility edges in the valence and conduction bands is called the ‘mobility gap’ fig (4.1.2) (Mott 1969).

![Figure 4.1.1: Optical absorption in amorphous semiconductor showing the interband region (I) and the urbach edge region (II).]
The absorption at slightly higher energies (associated with absorption coefficient $\alpha \geq 10^4$) may provide information on the combined density of states at the valence-band and conduction-band edges. There are two types of optical transitions that can occur at the edge of crystalline semiconductors, direct or indirect. The theory of such transitions has been presented by Davis and Mott (1970). Both involve the interaction of an electromagnetic wave with an electron in the valence band, which is raised across the fundamental gap to the conduction band. However, indirect transitions also involve simultaneous interaction with lattice vibrations. Thus the wave vector of an electron can change in the optical transition, the momentum change being taken or given up by photon. (The radiation imparts negligible momentum to the electron). In amorphous materials, account is essentially taken for the localized electronic states in the mobility gap.
The matrix element $D(E)$ for the optical transitions between states in different bands have the same value whether or not the initial and final states are localized. Also, the density of states at the band edges are assumed to be linear functions of the energy. Moreover, transitions are improbable whenever both initial and final states are localized (Davis and Mott, 1970).

Mott and Davis (1979) have reported, the general theory of the optical absorption of amorphous semiconductors.

The optical absorption coefficient $\alpha(v)$ at a given frequency is given by

$$\alpha(v) = \frac{4\pi\sigma_{\text{min}}}{Cn_0\Delta E} \cdot x \cdot \left(\frac{h\nu - E_{\text{opt}}}{h\nu}\right)^r \tag{4.24}$$

where,

$\sigma_{\text{min}}$ is the extrapolated dc-conductivity at $T = \infty$

$n_0$ is the refractive index

C is the velocity of light

$\Delta E$ is a measure of the extent of band tailing

$\nu$ is the photon energy

$E_{\text{opt}}$ is the optical energy gap

$r$ is a number which characterizes the transition process

$\frac{4\pi\sigma_{\text{min}}}{Cn_0\Delta E} = B$ is the constant

The reflectance can be calculated using the equation (Moss 1959) given by,

$$T = (1 - R)^2 \exp(-A) \tag{4.25}$$

where, $R$ is the reflectance,

$T$ is the transmittance and
A is the absorbance.

The relation between optical dielectric constant ($\varepsilon'$) and square of wavelength ($\lambda^2$) is given by (Bottcher 1952, Spitzer and Fan 1957).

$$
\varepsilon' = n^2 = \left[ \frac{1+\sqrt{R}}{1-\sqrt{R}} \right]^2
$$

$$
\varepsilon' = \varepsilon'_{\infty} - \frac{\varepsilon^2}{\pi C^2} \frac{N}{m^*} \lambda^2
$$  \hspace{1cm} (4.26)

where,

$\varepsilon'_{\infty}$ is dielectric constant at infinite frequency

e is the electronic charge,

$N/m^*$ is the ratio of carrier concentration to the effective mass.

C is velocity of light and

$\lambda$ is the wavelength.
References


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