Chapter – I

1. Introduction

1.1 Introduction and Definition of Composites

The recent modern technology requires a material with unique properties that cannot be satisfied by the conventional materials such as metal, metal alloys, ceramic and polymeric materials. This is especially true for composite materials that are needed for aerospace, EMI shielding, transportation, battery and sensor applications [1-3]. For example, researchers of electronic engineering are looking for structural materials that have environmental stability, low density, strong mechanical impact, stiff, abrasion and noncorrosive as well as tunable electrical conductivity and interesting redox properties associated with the chain nitrogen [4]. The electrical properties of the polymers can be improved substantially by secondary doping. Polymer compounds can be designed to achieve the particular conductivity required for a given application.

Materials properties combinations and ranges have been and are yet being extended by the development of composites materials. Generally speaking, a composite is considered to be any multiphase material that exhibits a significant propitiation of the properties of both constituent phases such that a better combination of properties is realized [5]. According to this principle of combination action, better property combinations are fashioned by the judicious combination of two or more distinct materials.

A composite, in the present context, is a multiphase material that is artificially made, as opposed to one that occurs or forms naturally. In addition, the constituent phases must be chemically dissimilar and separated by a distinct interface. Thus, most metallic alloys and many ceramic do
not fit this definition because their multiphase formation is a consequence of natural phenomena [6]. Normally most of the composites materials are composed of just two phases, one is termed the matrix, which is continuous and surrounds the other phase, often called the reinforcement. The properties of composites are function of the properties of the constituent matrix, their relative amounts and geometry of the dispersed reinforcement. “Dispersed phase geometry” in this context means the shape, size, distribution and orientation of the particles.

1.1.2 Classification of Composites: Composites materials is a material consist of two or more distinct phases and having bulk properties significantly differ from those of any of the constituents. The larger phase of the composite is called matrix phase and the smaller phase is termed as dispersed phase. The property of composites changes based on the types of filler added to it. The shape, size and orientation of the filler in matrix significantly effects on the physical and chemical properties of the composites.

1.1.3 Matrix phase: The primary phase, having a continuous character is called matrix. Matrix is usually more ductile, less hard and rigid phase. It holds the dispersed filler and shares a load with it. The physical and chemical properties of the two dissimilar components of the composites phase exploit its technological applications.

1.1.4 Dispersed (reinforcing) phase

The second phase is rooted in the matrix in a discontinuous manner and this phase is termed as dispersed phase. Dispersed phase is normally harder and stronger than the continuous phase, therefore it is also called reinforcing phase. The reinforcement of filler enhances the various properties of the composites such as mechanical, electrical, thermal, optical and magnetic.
The composite broadly classified based on the material structure and material matrix as shown in figure 1.1 and 1.2:

1.1.5 Classification based on structure

Figure 1.1 shows classification scheme for composites based on reinforcement

1.1.6 Particulate Composites

The matrix reinforced in particulate composites fabricate by dispersing particles into continuous phase. Composites materials consist of two or more individual constituents however one phase should be in particles form which builds the desired property required for the technological applications. One form of composites is particulate reinforced composites with concrete in a building construction being a good example where the aggregate coarse rock/gravels are
incorporated in cement [7]. The aggregate provides stiffness and strength while the cement acts as the binder to hold the structure together.

1.1.7 Fibrous Composites

1.1.8 Long-fiber reinforced composites (Continuous). Long-fiber reinforced composites consist of continuous fibers as a dispersive phase in the matrix. Thermoplastic long fiber are bulk molding materials are used in the matrix as a continuous fiber filaments running throughout end and significantly improve the mechanical strength, impact resistant, share load and temperature resistance over wide range. Heralded as an exciting growth area in thermoplastics long fiber composites are widely accepted as a viable alternative to traditional reinforced thermoplastics and metals for a vast array of applications. There are two types of long fiber thermoplastics as follows;

i. Unidirectional orientation of fibers.

ii. Bidirectional orientation of fibers (woven).

1.1.9. Short-fiber reinforced composites (Discontinuous). Short-fiber reinforced composites consist of short form of fibers dispersed in the continuous matrix which length may be less than 100 nm diameter. The intrinsic problems of these kind of fibers are produce micro-cracking at the end of matrix causes low strength and hardness and the fiber/matrix interface is often a limiting factor for improving mechanical properties of short fiber composites [8]. There are two types of short discontinuous fiber as follows;

iii. Composites with random orientation of fibers.
iv. Composites with preferred orientation of fibers.

1.1.9 **Structural Composites**: When a fiber reinforced composite designed with multilayer fiber oriented in different direction termed as an angleply composite. In production process various colour of composites with broad range of texture can be fabricate. Structural composite design practically eliminates the requirement of post-processing or painting, reducing the end cost of the finished part. Apart from these advantages of fiberglass parts include high dimensional stability, low vibration and high chemical resistance in corrosive applications.

i. Laminate      ii. Sandwich

1.2 **Classification based on Matrix**

![Classification Scheme for Composites Based on Matrix](image)

Figure 1.2 shows classification scheme for composites based on matrix
1.2.1. Metal Matrix Composites (MMC): Metal Matrix Composites are consists of a metallic continuous phase such as aluminum, magnesium, iron, cobalt, copper and a dispersed phase may be ceramic, oxides, carbides or metallic particles like lead, tungsten, molybdenum etc. The dispersive phase enhances the glassy nature of the surface, increase the chemical and thermal resistance, hardness and brittleness.

1.2.2 Ceramic Matrix Composites (CMC)

Ceramic Matrix Composites are composed of a ceramic matrix and incorporate fibers of other ceramic or oxide material as a dispersed phase. Generally, the embedded dispersive phase significantly effects on electronic property and changes tremendously its surface morphology. The size, shape and orientation of the dispersive phase decide the magnetic saturation and coherivity value of the composite materials.

1.2.3 Polymer Matrix Composites (PMC)

Polymer Matrix Composites are fabricated by using a matrix of thermoset such as unsaturated polyester (UP), epoxy (EP)) and thermoplastic like polyvinylchloride, polycarbonate (PC), nylon and polysterene. The embedded dispersive phase may be glass, carbon, steel or Kevlar fibers [9]. When the continuous phase and dispersive phase are two or more polymers mixed together to form a homogenous single phase materials with unique property is termed as blend. These blends are having high mechanical strength compare to industrial materials, good electrical and optical properties.
Based on electrical conductivity polymer matrix are further classified as:

i. Non-conducting polymer matrix composites

ii. Conducting polymer matrix composites

1.2.4 History of conducting polymer composites

The first report of polyaniline in mid 19th century after the discovery of aniline later on there are several reviews on conducting polymer composites field. Let hereby reported that the chemical and electrochemical oxidation of aniline forms polyaniline in acidic media, noting that reduced form was green colour where as the oxidized form is deep blue. In beginning of 20th century, the chemists from German prepared several compounds termed as "pyrrole black" and "aniline black" and used them industrially. Classically, such polymer "blacks" and their basic compound is polyacetylene and their co-polymer was termed as "Melanins" [10].

In early 1950s, researchers found that polycyclic aromatic compounds give semiconducting charge-transfer complex salts with halogens atom. While these complexes were not technically polymers but it is shows that the organic compounds can carry current. Organic conductors were intermittently before discussed on the bases of superconductivity phenomenon following the discovery of BCS theory [11-13].

The conductivity of iodine-doped polypyrroles was reported by Bolto and co-workers in 1963 and found the lowest resistivity of 0.03 Ω-cm with other organic conducting polymer composites. This resistivity is normally found in present-day efforts. The 1964 monograph Organic Semiconductors cites multiple reports of high-conductivity oxidized polyacetylenes, some with resistivity as low as .001 ohm-cm [14-16]. Subsequently, De Surville et al, showed a
high conductivity in a polyaniline and Diaz and Logan reported films of polyaniline that could acts as electrodes in the year of 1980 [17, 18]. In the year of 1960s Blois et al, reported that the semiconduction in melanins and further studied their physical properties [19]. Nicolaus et al. further defined the conductive polymer structures [20]. Classically, all polyacetylenes, polypyrroles and polyanilines are melanins and the simple melanin can be termed as acetylene-black [21].

1.3 Conducting Polymers

The conductive materials such as carbon black, carbon fibers, metal flakes, metal wire or fibers and so on is called as conductive polymer or the backbone polymers whose backbones are responsible for the generation, propagation and termination of charge carriers.

Classification of conducting polymer as follows; 1) Nature of polymer and dopant (figure 1.3) and 2) Conduction mechanism (figure 1.4).

1.3.1 Classification based on nature of polymer and dopant

![Diagram](image-url)

Figure 1.3 Classification for conducting polymer based on nature of matrix & dopant
In conjugated polymers the long chain carbon compounds contains alternate single and double bonds that leads to one unpaired electron per carbon atom [25]. In charge transfer polymers, the orbital on adjacent molecules are overlapped to form continuous one-dimensional bands. The charge carriers in this system are provided by the electron transfer between the electron donors (D) and acceptor (A) molecules. In this case, the conductivity arises from the ion migration between coordination sites repeatedly generated by the local motion of polymer chain segments [26]. Therefore, a desirable polymer host must possess: a) electron-donating atoms or groups for the coordinate bond formation with cations, b) low bond rotation barriers for an easy segmental motion of the polymer chain, and c) an appropriate distance between coordinating centers for multiple inter-polymer bonding with cations.

In the case of conductively filled polymers, the conductivity is introduced through the addition of the conducting components in various polymer materials including both amorphous and crystalline polymers which can be made electrically conducting.

1.3.2 Classification based on conduction mechanism

![Classification for conducting polymer based on conduction mechanism](image)

Figure 1.4 Classification for conducting polymer based on conduction mechanism
1.3.3 Conducting Polymer Composites

Conducting polymer composites are mixture or blends of conductive particles and polymers. Various conductors have been used in different forms together with large number of conducting and engineering plastics. These can be injection molded into desired shapes. Various conductive fillers have been tried such as carbon blacks, graphite flakes, fibers, metal powders etc. The electrical conductivity of the polymer is decided by the volume fraction of the filler. A transition from insulating to non-insulating behavior is generally observed when volume fraction of conductive filler in the mixture reaches a threshold of about 25%. The various polymers, which have been used as major matrix, are typically PC, PET, PP, Nylon, PVC, HDPE etc.

1.3.5 Organometallic Polymeric Conductors

These types of conducting materials are obtained by adding organometallic groups to polymer molecules. In this type of materials, the d-orbital of metal may overlap \( \pi \)-orbital of the organic structure and thereby increases the electron delocalization. The d - orbital may also bridge adjacent layers in crystalline polymers to give conducting property to it. Metallophthalocyanines and their polymers fall in this class of polymeric material [27]. These polymers have extensively conjugated structures. The bridge transition metal complexes form one of the stable systems exhibiting intrinsic electrical conductivities without external oxidative doping.
1.3.6 Polymeric Charge Transfer Complexes

Polymeric Charge Transfer Complexes (CTC) are formed when acceptor like molecules are added to the insulating polymers. There are many charge transfer complexes reported in the literature, e.g. CTC of tetrathiafulvalene (TTF) with bromine, chlorine etc [28]. The reason for high conductivity in polymeric charge transfer complexes and radical ion salts are still somewhat obscure. It is likely that in polymeric materials, the donor – acceptor interaction promotes orbital overlap, which contributes to alter molecular arrangements and enhances electron delocalization.

1.3.7 Inherently Conducting Polymers

Research in the field of inherently conducting polymer started nearly three decades ago when Shirakawa and his group found drastic increase in the electrical conductivity of polyacetylene films when
exposed to iodine vapor [29]. Following this breakthrough, many small conjugated molecules were found to polymerize, producing conjugated polymers, which were either insulating or semiconducting in the oxidized or doped state. These conjugated polymers are studied as the intrinsically conductive polymers. The electronic properties of these polymers are due to the presence of π-electrons and the wave functions of which are delocalized over long portions of polymer chain when the molecular structure of the backbone is planar [30]. Hence it is necessary that there are no torsion angles at the bonds, which would decrease the delocalization of the π-electron system. Some of the examples of conjugated polymers are shown in the figure 1.6 below and the features, which differentiate, conjugated polymers from conventional polymers are as follows:

![Schematic representations of conjugated polymers](image)

- Band gap $E_g$ (electronic band gap) is small (~1 to 3.5 eV) with corresponding to low excitations and semiconducting behavior.
- Can be oxidized or reduced through charge transfer reactions with atomic or molecular dopant species.
- Net charge carrier mobilities in the conducting state are large enough and because of this, high electrical conductivity is observed.
Quasiparticle, which under certain conditions, may move relatively freely through the material. The electrical and optical properties of these kinds of materials depend on the electronic structure and on the chemical nature of the repeated units. The electronic conductivity is proportional to both density and the drift mobility of the charged carriers. The carrier drift mobility is defined as the ratio of the drift velocity to the electric field and reflects the ease with which carriers are propagated. To enhance the electrical conductivity of polymers, an increase in the carrier mobility and the density of the charge carriers is required [31].

1.4. Conjugated Conducting Polymers

1.4.1. Structure and Properties

Conducting polymers are extensively conjugated molecules: they have alternating single and double bonds. In these molecules, electrons are able to move from one end of the polymer to the other through the extended π-orbital system [32]. Hence CPs is known to be either semiconductors or conductors, which are related to how bands and shells of electrons form within a compound. In view of the electronics of ECPs, the Band theory is employed to explain the mechanisms of conduction in CPs. The theory originates from the formation of energy bands in polymer materials from discrete orbital energy levels found in single atom systems. In this regard, it is vital to review band theory [33].

1.4.2 Band theory of CPs

The approach of physical chemistry explains a band theory which relates to the atomic structure of quantum theory. The quantum theory successfully explained the atomic spectra of hydrogen atom [8].
Quantum mechanics introduced an important concept which explained that atoms could only occupy well-defined energy states and for isolated atoms the energy states were very sharp [34]. The spectral emission lines which resulted correlated to electrons jumping from one allowed energy state to another and this gave rise to correspondingly narrow line widths. In a crystalline solid, atoms cannot be viewed as separate entities, because they are in close proximity with one another, and are chemically bonded to their nearest neighbor [35]. This leads to the concept that an electron on an atom sees the electric field due to electrons on other atoms and the nature of the chemical bond implies that electrons on close-neighbour atoms are able to exchange with one another, causing the broadening of sharp atomic energy states into energy ‘bands’ in the solid [36].
Figure 1.7 Formation of bands in a conducting solid in the 3rd period and overlap between the valence and conduction bands.

This can be illustrated using an example below in figure 1.7, that depicts 3p and 3s electron shells for a single metallic atom in the third period of the periodic table that overlap to become bands that overlap in energy (Atkins, 2002) [37]. The association of these bands is no longer solely with single atoms but rather with crystal as a whole. In other words, electrons may appear with equal probability on atoms anywhere else in the crystal.

The energy band that results from the bonding orbitals of a molecule is known as the valence band, while the conduction band is as a result of the antibonding orbitals of the molecule. The width of individual bands across the range of energy levels is called band width. The valence band (VB) represents the highest occupied molecular orbital (HOMO) and the conduction band (CB) represents the lowest unoccupied molecular orbital (LUMO) [38]. The gap between the highest filled energy level and lowest unfilled energy level is called band gap ($E_g$). This band gap represents a range of energies which is not available to electrons, and this gap is known variously as ‘the fundamental energy gap’, the ‘band gap’, the ‘energy gap’, or the ‘forbidden gap. The level of electrons in a system which is reached at absolute zero is called the Fermi level ($F_L$) [39]. It has been demonstrated that in order to allow the formation of delocalized electronic states, CPs molecular arrangement must be conjugated [40]. The delocalization of the electronic states relies on the resonance stabilized structure of the polymer. The size of the energy band gap depends on extend of delocalization and the alternation of double and single bonds. Moreover the size of the energy band gap will determine whether the CP is metal, semiconductor or insulator [41]. Combining the concepts explained in both atomic and molecular orbital
theory, the electronic properties of metals, semiconductors, and insulators can be differentiated with reference to the energy band gap as shown in figure 1.8 below.

![Figure 1.8 Energy band diagram demonstrating band gaps](image)

In metals there is no range of energies which is deemed unavailable to electrons, which simply means that forbidden gap or band gap in metals is $E_g = 0 \text{ eV}$. Hence metals always have a partially filled free-electron band, because the conduction and valence bands overlap. Hence the electron can readily occupy the conduction band. Insulators have a band gap which is larger than 3 eV [42], the energy gap between VB and CB is too large, hence the electron is not able to make that jump to detach from its atom, in order to be promoted to the valance band. Consequently they are poor electrical conductors at ambient temperatures. Insulators can be defined as materials in which the valence bands are filled and the forbidden energy gap between valence band and conduction band is too great for the valence electrons to jump at normal temperatures from VB to the CB [43].

### 1.4.2 Solitons, Polarons, Bipolarons and Band Structures of Intrinsically Conducting Polymers
The band structure of trans-(CH), assuming an idealized linear one dimensional molecules, can be regarded as being developed as shown diagrammatically in table 2.1, in which the bonding molecular orbitals are $\frac{1}{2}$ orbitals and antibonding molecular orbitals are $\frac{3}{4}$ orbitals. The formation of filled $\frac{1}{4}$ band 20 (valence band) can be regarded as by joining together of (CH) units containing an unpaired P$\frac{1}{4}$ electron.

Addition of electrons to the conduction band or removal of electrons from the valence band cause a change in the energy level of these bands which results in the formation of new bands. Since trans-(CH), has a doubly degenerate ground state, i.e., the energy of the molecule is the same regardless of the phasing of the double bonds, one new band is formed in the middle of band gap when the number of electrons in the $\frac{1}{4}$ system of the molecule is changed. Removal of electron from valence band (oxidation of the $\frac{1}{4}$ system, p-doping) results in the formation of an empty band, i.e., positive “soliton” band in the band gap. Addition of electron to the conduction band (reduction of the $\frac{1}{4}$ system, n-doping) results in the formation of a filled band, i.e., negative “soliton” band in the band gap [44].

If a conjugated polymer such as poly(paraphenylene) does not have a degenerate ground state, two new bands will be formed in the band gap when the number of electron in the $\frac{1}{4}$ system is changed. The upper band in the band gap lies under the bottom of conduction band while the lower band lies above the top of valence band. If the lower band is half filled (p-doping), it is called positive “polaron” band. If the upper band is half filled (n-doping), it is called negative “polaron” band. When both lower band and upper band are empty (p-doping), it is called positive “bipolaron” band [45]. When both lower and upper bands are filled (n-doping), it is called negative “bipolaron” band. A given polymer may consist of polarons at one doping level and bipolarons at a different doping level or consist of significant amounts of polarons and bipolarons with each other under certain conditions.
Table 1 presents both physical and chemical terms of the defects mentioned above.

<table>
<thead>
<tr>
<th>Physical terms</th>
<th>Chemical terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-doped state</td>
<td>Undisturbed conjugation</td>
</tr>
<tr>
<td>Neutral soliton</td>
<td>Free radical</td>
</tr>
<tr>
<td>Positive soliton</td>
<td>Carbocation</td>
</tr>
<tr>
<td>Negative soliton</td>
<td>Carbanion</td>
</tr>
<tr>
<td>Positive polaron</td>
<td>Radical cation</td>
</tr>
<tr>
<td>Negative polaron</td>
<td>Radical anion</td>
</tr>
<tr>
<td>Positive bipolaron</td>
<td>Carbodication</td>
</tr>
<tr>
<td>Negative bipolaron</td>
<td>Carbodianion</td>
</tr>
</tbody>
</table>

1.4.3. Polyaniline

Intrinsic conducting polymers (ICPs) have been used in numerous applications such as corrosion protection, [46] microelectronics, [47] and chemical sensing [48]. ICPs, including polyacetylene, polythiophene, polypyrrole and polyaniline, are conjugated polymers, in which single and double bonds are alternated on the polymer chain providing high electron density. The polymers possess high electron density and the pristine forms have low conductivities, usually in the range of an insulator or a semiconductor. High conductivity of the polymers can be achieved through the reduction or oxidation of the polymers with the uptake of either an electron donor or acceptor [49]. This process is called doping, changing the electrons density in the polymer backbone while providing charge mobility. The doped
forms of the polymers have high conductivity, which can be comparable to metals. Among other ICPs, polyaniline (PANI) is unique because the conductivity can be achieved through either protonation or anion uptake in the polymer. In contrast to other polymers, PANI doped with protons does not change the number of the electrons on the polymer backbone. This unique conductivity sets PANI apart from other conducting polymers. In addition, the thermal stability and ease of synthesis make PANI one of the most studied conductive polymer systems [50]

1.4.5 Properties of polyaniline

It has been previously demonstrated that the polyaniline chain can be formed by various combinations of the two repeating units known as the X and Y components of polyaniline [51]. Owing to this, PANI has many unique properties and electronic conduction mechanisms that distinguish it from the rest of the conducting polymers.
For example, the conductivity of PANI varies with the extent of oxidation (variation in the number of electrons) and the degree of protonation (variation in the number of protons).

Among the various oxidation states that PANI can exist in, the one that can be doped to a highly conductive state is the moderately oxidized emeraldine base [52]. This form of PANI has a structure which consists of equal proportions of amines (–NH–) and imine (=N–) sites. Through protonic acid doping, imine sites are protonated by acids HA to the bipolaron (dication salt) form [53]. The bipolaron then undergoes a further rearrangement to form the delocalized polaron lattice which is a polysemiquinone radical-cation salt as shown in figure 1.9. The resulting emeraldine salt has conductivity on a semiconductor level of the order of 100 S cm⁻¹, which is many orders of magnitude higher than that of common polymers (<10⁻⁹ Scm⁻¹) but lower than that of typical metals (>10⁴ Scm⁻¹) [54]. Only 1% of the charge carriers which are available in the ES salt actually contribute to its observed conductivity. If all the available charge carriers were to contribute, the resulting conductivity at room temperature would be ~ 10⁵ Scm⁻¹, which is comparable to that of copper [55].

The polyanilines, probably the earliest known synthetic polymer, [56, 57], refer to a large class of conducting polymers which have the following general formula as shown in figure 1.10.
A large variety of derivatives can be prepared through substitution in the ring or on the N atoms. One of the special properties of polyaniline is that it can be doped by protonic acids. Thus, the properties of the doped polymer can be turned by incorporating different dopant anions [58].

It has been found that polyaniline can exist in three different, isolable oxidation states at the molecular level [59]. They are the leucoemeraldine oxidation state, the emeraldine oxidation state, and the pernigraniline oxidation state. Other oxidation states are the result of physical mixture of these oxidation states. (i) Leucoemeraldine base: the fully reduced form of non-doped polyaniline. It is composed solely of reduced units as shown in 1.11 (a).

![Figure 1.11 (a) shows the structure of Leucoemeraldine base](image)

(ii) Pernigraniline base: the fully oxidized form of non-doped polyaniline. It is composed solely of oxidized base units as shown 1.11 (b).

![Figure 1.11 (b) shows the structure of pernigraniline base](image)

(iii) Emeraldine base: the intermediate oxidation state of polyaniline. It is composed of equal amounts of alternating reduced base & oxidized base units as shown 1.11 (c).
Conjugated organic polymers are either electrical insulators or semiconductors. These polymers can become highly electrically conductive by introducing a structural modification process called “doping”. Doping can be simply regarded as the insertion or ejection of electrons [60]. Doping process results in changes in the electrical and structural properties of the polymer. Doping of conducting polymer involves random dispersion or aggregation of dopants in molar concentrations in the disordered structure of chains and fibrils. The dopant concentration may be as high as 50%. Incorporation of the dopant molecules in the quasi one dimensional polymer systems also considerably disturbs the chain order leading to reorganization of the polymer [61]. Doping process is reversible and it produces the original polymer with little or no degradation of the polymer backbone. Both doping and undoping processes, involving dopant counterions which stabilize the doped state, may be carried out chemically or electrochemically. Doping of polymer leads to the formation of conjugation defects, viz. solitons, polarons or bipolarons in the polymer chain [62, 63]. The ultimate conductivity in polymeric semiconductors depends on many factors, viz. nature and concentration of dopants, homogeneity of doping, carrier mobility, crystallinity and morphology of polymers. By adjusting the doping level, [64] conductivity anywhere between that of the undoped (insulating or semiconducting) and that of the fully doped (highly conducting) form of the polymer can be easily obtained.

Generally in conducting polymers p-type doping is conducted with an electron acceptor, such as I₂, and n-type doping is conducted with donor species, such as Li. In the doped state, the backbone of a
conducting polymer consists of a delocalized system [65]. In the undoped state, the polymer may have a conjugated backbone such as in trans-(CH)_x, which is retained in a modified form after doping, or it may have a non-conjugated backbone, as in polyaniline (leucoemeraldine base form), which becomes truly conjugated only after p-doping, or a nonconjugated structure as in the emeraldine base formed of polyaniline which becomes conjugated only after protonic acid doping.

1.5.1. *Types of Doping*

1.5.1.1 *Redox doping*

All conducting polymers e.g., PPy, PT, PANI etc undergo p- and / or n- redox doping by chemical and / or electrochemical processes during which the number of electrons associated with the polymer backbone changes. The p-Doping is accompanied by partial oxidation of the backbone of the polymer [66]. It was first discovered by treating trans-(CH)_x with an oxidizing agents such as iodine and p-Doping can also be done by electrochemical anodic oxidation.

1.5.1.2. *Photo doping*

When trans-(CH)_x is exposed to radiation of energy greater than its band gap, electrons are promoted across the gap and polymer undergoes photo-doping.

1.5.1.3. *Non redox doping*
More recently, a non-redox doping process which neither involves adding nor removing electrons from the polymer backbone has been discovered [67]. For instance, a form of polyaniline (emeraldine base) can be doped by a non-redox process [68] which is accomplished by simply protonating the imine nitrogen atoms of the polymer to produce a polysemiquinone radical cation in which both charges and spin are delocalized along the polymer backbone. The conductivity of the polymer increases from $10^{-10}$ S/cm to 100 S/cm. This protonic acid doping process has subsequently been extended to poly(heteroaromatic vinlylens) and its derivatives [69]. It should be noted that the non-redox doping of emeraldine base (EB) is not limited to protonic acid dopants. For example, alkylating agents such as $(\text{CH}_3)_2\text{SO}_4$, have been used as “pseudo protonic acid” doping of EB, in which, the $\text{CH}^{+3}$ in $(\text{CH}_3)_2\text{SO}_4$ acts as if it were $\text{H}^+$ with respect to its addition to the imine nitrogen [70].

1.5.1.4. Doping Agents

Dopants may be classified as (a) Neutral dopants, (b) Ionic dopants, (c) Organic dopants, and (d) Polymeric dopants (e) Metal oxides dopants.

(a) Neutral dopants: $\text{I}_2$, $\text{Br}_2$, $\text{AsF}_2$, $\text{Na}$, $\text{K}$, $\text{H}_2\text{SO}_4$, $\text{FeCl}_3$

(b) Ionic dopants: $\text{LiClO}_4$, $\text{FeClO}_4$

(c) Organic dopants: $\text{CF}_3\text{COOH}$, $\text{CF}_3\text{SO}_3\text{Na}$

(d) Polymeric dopants: PVS, PPS, PS-co-MA

(e) Metal oxides dopants: $\text{WOn}_3$, $\text{CeO}_2$, $\text{Co}_2\text{O}_3$, $\text{SnO}_2$, $\text{TiO}_2$

Neutral dopants are converted into negative or positive ions with or without chemical modifications during the course of doping. Ionic dopants are either oxidized or reduced by an electron transfer with
the polymer and the counter ion remains with the polymer to make the system neutral [71, 72]. Organic
dopants are anionic dopants, generally incorporated into polymers from aqueous electrolytes during
anodic deposition of the polymer. Polymer dopants are functionalized polymer electrolytes containing
amphiphilic anions [73]. Metal oxide dopants are known for their electron donor property. Since the
oxygen atoms of the metal oxide contains lone pairs of electrons, this in turn helps localization of charge
in the polymeric chain, leading to the enhancement of conductivity of the host polymer.

1.6. Effect of Doping on Conductivity.

The doping process involves transfer of the charge to or from the bonding system of the
conjugated polymer, leaving the system essentially intact and hence the structural identity of an
individual chain is preserved. However, vibrational, electronic and other properties of the polymer are
strongly altered upon doping. The most interesting result of the doping is the increase of the polymer
conductivity over several orders of magnitude. In some cases, conjugated polymers reach the
conductivity of metals with a negative temperature coefficient which is characteristic of metallic
behavior [74-77]. Doping with acceptor or donor molecules causes a partial oxidation (p-doping) or
reduction (n-doping) of the polymer molecule. As a result, positively or negatively charged quasi-
particles are created presumably polarons in the first step of doping. When doping proceeds, reactions
among polarons take place, leading to energetically more favorable quasi-particles, ie a pair of charged
solitons (bipolarons) in materials with a degenerate ground state [78]. Thus due to the changes in the
environment of the chains, disorders are created from doping. At low dopant concentration, the dopant
molecules occupy random positions between the chains. They affect the electronic properties by their
coulomb potential and by hybridization with the polymer p-orbital [79]. As polarons produced has long
lifetime, they are treated as quasi-particles. Polaron have low mobility, which results in obtaining
moderate conductivity at low doping concentration. As the doping level is increased, the concentration of polarons goes up and they become crowded together, close enough to form bipolaron [80-83]. At this point in the doping process, conductivity undergoes a marked increase. Once the radical components of the polarons have combined to form bonds, the remaining charges achieve high mobility along the chain.

1.6.1 Application of conducting polymers.

PANI is a diverse material which has been utilized in applications including batteries, electronics, and biological applications. Emeraldine base has been used to produce cathodes for batteries that have better recyclability compared to batteries with polyacetylene cathodes. [84] In addition, PANI and its derivatives have been utilized as coatings for metals such as iron and stainless steel to prevent corrosion. [85] PANI is a promising material for electronic devices such as diodes or transistors because of the change in conductivity under the applied potential. Xing and co-workers have produced a PANI diode which is currently being optimized for improved efficiency and reproducibility. [86] Moreover, PANI can be deposited on Au microelectrodes to produce high quality transistors. The transistors exploit the properties of PANI which can be oxidized or reduced in response to electrical or chemical signals. When a potential is applied, it rapidly transfers charges in between the electrodes in an electrolyte producing switching time of less than 0.1 s. [87] In addition, since PANI can be doped/de-doped by acids and bases, it is a promising material for gas sensors. [88] The detection of gases such as ammonia is based on the change in conductivity of PANI when it is exposed acidic or basic gases. Moreover, incorporation PANI with other materials expanded its use to biological applications, which is typically excluded due to the high pH. For example, the modification of PANI with enzymes such as horse peroxidase, [89] cytochrome c, [90] glucose oxidase, [91] or single-stranded DNA [92] fabricates biosensors for detecting \( \text{H}_2\text{O}_2 \), glucose, and monitoring DNA hybridization, respectively.
1.6.2. Introduction to Metal Oxides

Many of the $A_2B_4O_4$-type crystals have the $\beta-K_2SO_4$ type structure. Since the subgroup is polar, the family of crystal has been investigated widely as a candidate of ferroelectrics. However, these crystals have not necessarily the same succession of the phase transition. According to an empirical rule about the ratio the ionic radius of $A^+$ to the average bond length $B-O$ in the $BO_4$ $2^-$ tetrahedron, $r(A)/r(BO)$ [93], Ferrite crystallises in the monoclinic system, space group $C_2/m$, with unit-cell dimensions $a= 12.348$, $b= 6.081$, $c= 7.538$ Å, and $\beta= 115.74^\circ$. Its structure, determined by three-dimensional Patterson and Fourier syntheses and refined by least-squares techniques contains isolated, almost regular $MoO_4$ tetrahedra with average $Mo-O$ distance $1.76 \pm 0.01$ Å and potassium ions occupying eight coordinate positions [94]. The potassium–oxygen co-ordination may be described basically as somewhat distorted trigonal prismatic, where the $K-O$ distances are all $<3$ Å, with the co-ordination polyhedron completed by two longer contacts of $3.21$ Å. The similarity to the $\beta-K_2SO_4$ structure is discussed; $K_2WO_4$ and $[NH_4]_2MoO_4$ have been shown to be isomorphous with $K_2MoO_4$. [95-99].

In the present study the following transition metal oxides are used.

- Zinc ferrite ($ZnFe_2O_4$)
- Nickel ferrite ($NiFe_2O_4$)

1.7 Literature Review:

1) Jiaheng Wang et al., [100] reported the paraffin-bonded $ZnFe_2O_4/SiO_2/PANI$ (ZSP) nanocomposite rings was fabricated with different orientations of the simple magnetization planes of the ZSP disks in the paraffin binder in order to determine the effect of directional orientation of the easy magnetization planes on their electromagnetic properties. The magnetization planes induced by shape anisotropy and oriented by a magnetic field in the
vertically oriented ring result in a general enhancement in permeability of 7–60% in the broad UHF–Ku (0.1–18 GHz) bands, while those in the horizontally oriented ring lead to a significant enhancement of 58–1100% in the low-frequency L and S (1–4 GHz) bands, in comparison with the randomly oriented ring. The results of permeability good agreements with the theoretical prediction based on the Landau–Lifshitz–Gilbert equation and the Bruggeman’s effective medium theory. The dipolar polarizations in the different oriented rings give rise to 3–11% improvement and weakening in permittivity, respectively, in compared to the randomly oriented ring. The improvement in permeability also broadens the electromagnetic wave absorption in all oriented rings, especially in the L and S bands for the horizontally oriented ring.

2) Qiaoyun Zhao et al., [101] studied the ZnFe$_2$O$_4$·Fe$_2$O$_3$/PANI nanocomposite was prepared through a simple co-precipitation technique. Then ZnFe$_2$O$_4$·Fe$_2$O$_3$ was doped with polyaniline (PANI) via UV-assisted chemical oxidation polymerization to fabricate the nanocomposite photocatalysts. Besides, the effect of the aniline amount on composition, absorption, morphology and photocatalytic efficiency of the composite photocatalysts was investigated. The results show that with the increase of the amounts of aniline in the preparation process the composites present various morphologies including small nanoparticle, big granular nanoparticle, and nanofiber. At the same time, the content of PANI in the nanocomposite is enhanced visible light-harvesting ability and photocatalytic activity under visible light irradiation. The degradation rate of rhodamine B (RhB) was up to 75.5% after 120 min. Ferromagnetism makes ZnFe$_2$O$_4$·Fe$_2$O$_3$/PANI susceptible to magnetic field and easy to be collected magnetically for iterative use. 64.4% RhB was degraded when the photocatalyst was used after 4 times.

3) G. D. Prasanna et al., [102] reported inexpensive one-step in-situ polymerization method of polyaniline/ZnFe$_2$O$_4$ nanocomposites at different weight percentages. These results reveal the
formation of polyaniline/ZnFe$_2$O$_4$ nanocomposites. The morphology of these samples is studied by scanning electron microscopy. Further, the ac conductivity ($\sigma_{ac}$) of these nanocomposites is investigated in the frequency range of 1 kHz–10 MHz. The presence of polarons and bipolarons are responsible for the frequency dependence of ac conductivity in these nanocomposites. The ac conductivity is observed to be constant up to 1MHz and thereafter it enhanced steeply. The ac conductivity of 40 wt% of nanocomposites shows highest value of 0.695 Scm$^{-1}$ at room temperature.

4) Ramesh Patil et al [103] reported polyaniline composites with different weight percentages of ZnFe$_2$O$_4$ in PANI were prepared by chemical oxidative polymerization of monomer aniline. From the infrared spectroscopy (FTIR) studies on polyaniline/ZnFe$_2$O$_4$ composites, the peak at 1140 cm$^{-1}$ is considered to be measure of the degree of electron delocalization and also the Vander walls interaction between polymer and zinc ferrite. The results of ac conductivity show a strong dependence on the weight percent of ZnFe$_2$O$_4$ in polyaniline. At higher frequency, conductivity ($\sigma_{ac}$) increases because of hopping of polarons from one localized states to another localized states. It is observed from the electrical conductivity studies that the 30 wt.% of ZnFe$_2$O$_4$ in the polymer matrix shows the enhancement of the conductivity of the polyaniline and their values are found to be in the semiconducting range. $\varepsilon''$ shows a dielectric loss characterized by relaxation frequency for all the samples. It decreases almost linearly in all the composites, after 1 kHz frequency $\varepsilon''$ exhibits low value plateau. It is observed that the imaginary part of the impedance is start to decrease from low frequency and reaches an asymptotic value in the high frequency range and thus the HCl doping is decreasing the impedance of the sample.
5) S. Mikhaylov et al. [104] reported that the dodecylbenzenesulfonic acid (DBSA) doped in polyaniline and the dispersion in chlorobenzene (CB) and dichloroacetic acid (DCAA) effects on the morphology and sensing properties of TiO$_2$/PANI-DBSA hybrid nanocomposite layers cast on transducer electrodes. The obtained results evidence that these effects are caused by the solubility of the PANI of the prepared nanocomposites in the solvents and the boiling temperature of the latter. To estimate a quantitative effect of PANI, we used PANI-DBSA composites to determine the PANI polymerization yield. The highest magnitudes and rates of the sensor responses to gaseous ammonia are shown by the nanocomposite layer with an intermediate PANI-DBSA content (18.9 wt%) and cast from the nanocomposite dispersion in CB. We explain this effect by the specific morphology of the layer, which appears to be due to the poor solubility of the PANI-DBSA component in this solvent. The comparison of sensitivity of the chemically synthesized nanocomposites to ammonia with that of their mechanically mixed analogs demonstrates the better sensing performance of the former.

6) Rajeev Jain et al. [105], reported a novel polyaniline–graphene oxide nanocomposite (PANI/GO/GCE) sensor has been fabricated for quantification of a calcium channel blocker drug levamlodipine (LAMP). Fabricated sensor has been characterized by electrochemical impedance spectroscopy, square wave and cyclic voltammetry, Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The developed PANI/GO/GCE sensor has excellent analytical performance towards electrocatalytic oxidation as compared to PANI/GCE, GO/GCE and bare GCE. Under optimized experimental conditions, the fabricated sensor exhibits a linear response for LAMP for its oxidation over a concentration range from 1.25 µg mL$^{-1}$ to 13.25 µg mL$^{-1}$ with correlation coefficient of 0.9950 ($r^2$), detection limit of 1.07 ng mL$^{-1}$ and quantification limit of 3.57 ng mL$^{-1}$. The sensor shows an excellent performance for detecting LAMP with
reproducibility of 2.78\% relative standard deviation (RSD). The proposed method has been successfully applied for LAMP determination in pharmaceutical formulation with a recovery from 99.88\% to 101.75\%.

7) J. N. Ansari et al [106] reported that Polyaniline–Nd\textsubscript{2}O\textsubscript{3}:Al\textsubscript{2}O\textsubscript{3} nanocomposites were prepared by in situ oxidative polymerization method using different weight percentages of oxide powders. The electrical conductivity of the nanocomposites increases with increase in temperature as well as with concentration of Nd\textsubscript{2}O\textsubscript{3}:Al\textsubscript{2}O\textsubscript{3} particles in polyaniline. This is because of the hopping of charge polarons and extended chain length of the nanocomposites as evidenced by the negative thermal coefficient (NTC) characteristic. A high NTC value of 2.67 was found in nanocomposites with 15 wt\% of oxide particles. These nanocomposites show low dielectric constant and dielectric loss; the electrical conductivity is higher than 0.3 S/cm as confirmed by Cole–Cole plot that indicates a decrease in both grain resistance and bulk resistance of the nanocomposites. The current–voltage and capacitance–voltage measurements were also carried out. The carrier mobility $\mu$ values of pure polyaniline and nanocomposites were found to be $4.27 \times 10^{-3}$ and $1.45 \times 10^{-2}$ H.M, respectively. A significant enhancement in carrier mobility was observed in comparison with the literature.

8) Nacer Badi et al [107] The graphene, a monolayer of carbon atoms arranged in two dimensional lattices has attracted greater research interests due to its exceptional electrical and optical properties. The properties of conducting polymer can be tailored to a large extent with a suitable formation of nanocomposites using graphene material. In this paper we report on the preparation and characterization of transparent conductive graphene nanoplatelets/polyaniline (GNPs-PANI) composite coatings. The structural features of the nanocomposite were investigated using Fourier transform infrared spectra (FTIR) and micro Raman analysis. FTIR
spectra of GNP-PANI coating clearly reveal the presence of characteristic peaks of both PANI and GNP indicating the formation of a composite film. The micro Raman spectra reveal the presence of characteristic D and G modes of vibrations in composite film (GNP-PANI) with intensity of G mode greater than the D mode due to the composite formation. The optical Raman images confirm the uniform dispersion of GNP in PANI. The transport properties of the composite film were studied through AC/DC conductivity measurement, dielectric behavior is analyzed with respect to dielectric constant, loss tangent, and Cole-Cole plots characteristics. The study of transport properties of the composite film reveals that the presence of GNP in the PANI significantly tailors the electrical properties of pure PANI. Due to its transparent nature and excellent electrical properties, these GNP-PANI nanocomposites can find wide technological applications in the fabrication of optoelectronic devices.

9) M T S Chani et al [108] reported that the fabrication and investigation of humidity sensors based on orange dye (OD) and polyaniline (PANI) composite films. A blend of 3 wt.% OD with 1 wt.% PANI was prepared in 1 ml water. The gap between the electrodes was 45 μm. The sensing mechanism was based on the impedance and capacitance variations due to the absorption/desorption of water vapor. It was observed that with the increase in relative humidity (RH) from 30% to 90%, the impedance decreases by $5.2\times10^4$ and $8.8\times10^3$ times for the frequencies of 120 Hz and 1 kHz, respectively. The impedance—humidity relationship showed a more uniform change compared to the capacitance—humidity relationship in the RH range of 30% to 90%. The consequence of annealing, measuring frequency, response and recovery time, and absorption—desorption behavior of the humidity sensor were also discussed in detail. The annealing resulted in an increase in sensitivity of up to 2.5 times, while the measured response
time and recovery time were 34 s and 450 s, respectively. The impedance—humidity relationship was simulated.

10) A Parveen et al [109] prepared polyaniline-CaTiO$_3$ nanocomposites with their various weight percentages by chemical oxidative in situ polymerization technique. Humidity sensor properties of polyaniline-CaTiO$_3$ nanocomposite show better sensing properties and exhibit good linearity in sensing response curve, which discuss the implications of distortions and nonstoichiometry on their physical properties. Among all composites, 50 wt % of polyaniline-CaTiO$_3$ nanocomposites show high sensitivity up to similar to 90% and their response-recovery times are 500 and 453 s, respectively.

11) Jingping Wang et al, [110] reported that the One-dimensional nanostructured polyaniline (1D nano-PANI), including nanofibers, nanowires, nanobelts, nanotubes, nanorods, nanoneedles, and nanosticks, has been extensively studied recently due to its unique properties and many potential applications. Newly invented chemical methods for fabrication of 1D nano-PANI, such as solid-state polymerization, seeding polymerization, UV light- and microwave-assisted polymerization, plasma-induced polymerization, porous membrane controlled polymerization, and vapor phase polymerization, are briefly reviewed, and morphology controlling of the nanostructures during several synthesizing processes are reported and discussed at first. The formation mechanisms and key factors that affect the morphology evolution of the 1D nano-PANI are discussed. Novel features of 1D nano-PANI, such as aligned or oriented, longer, self-doped, chiral, derivative, carbonized, and dendritic PANI, are summarized. Finally, newly exploited applications of 1D nano-PANI in the past few years, such as sensors (e.g., gases sensors, biosensors, moisture or humidity sensors, TNT sensors, taste sensors, and noble metal ion sensors), absorbents, catalysts, actuators, supercapacitors, batteries, fuel cells, solar cells,
electrochromic devices, hydrogen storages, surface modifiers, field-effect transistors, and functional materials etc.

12) Rahul S. Diggikar et al [111] designed and successfully synthesized nanocomposites (NCs) of silver vanadium oxide nanospheres dispersed in different ultrathin layers of polyaniline (PANI-β-AgVO₃) at different temperatures (60 and 80 °C) by in situ chemical oxidative polymerization for the first time. The NCs synthesized at temperatures of 60 and 80 °C show approximately 4 and 2 nm ultrathin layers of PANI grown on SVO nanospheres, respectively. The sizes of the SVO nanospheres dispersed in the ultrathin PANI layers are in the range of 10–40 nm. The NCs are further characterized by ultra violet-visible (UV-vis) spectroscopy. The SVO dispersed in a layer of PANI NC exhibits excellent humidity sensing characteristics. The response and recovery times are found to be 4 and 8 seconds, respectively. The NCs have good potential as supercapacitors as well as in fast responsive humidity sensors.

13) Q. Liang et al [112] studied that the Micro humidity sensors are fabricated by radio-frequency sputtering ZnO and In₂O₃ thin films on SiO₂/Si substrates with interdigitated Pt signal electrodes. By adjusting the sensing film form, the micro sensors with a tiny area (1.36 mm × 0.55 mm) exhibit controllable humidity sensing properties. The best sample is obtained by sputtering two times of ZnO and one time of In₂O₃ on sensor active area (0.63 mm × 0.55 mm). The corresponding impedance changes by more than four orders of magnitude over the whole testing humidity range (from 11% to 95% relative humidity), and the response and recovery times are about 15 s and 40 s, respectively. High stability and good consistency are also observed based on the as-fabricated sensors. The improved and excellent humidity sensing properties are explained by the hetero junctions between ZnO and In₂O₃ thin films. High sensor performance
and large-scale fabricating potentiality demonstrate that the micro humidity sensors are very promising devices for humidity detection which could be produced at industrial level.

14) Husnu Cankurtaran et al [113] reported that a water soluble conductive polymer, poly(diphenylamine sulfonic acid) was synthesized by using both chemical (PSDA) and electrochemical (EPSDA) polymerization. The effects of film composition, applied potential bias, alternating current frequency and polymer film thickness on electrical properties and sensitivity were determined. PSDA-b-PEG films showed high humidity sensitivity, i.e. the impedance ranged about four orders of magnitude over the relative humidity range between dry and saturated humid conditions under 0.2 V of potential bias and 100 kHz of alternating current frequency. The thin film sensor of PSDA-b-PEG copolymer has a linear response in the range from 0 to 95% relative humidity. The repeatability of the sensor responses was good enough, i.e. the relative standard deviation was less than 3% and 4% at the lowest and highest humidity levels, respectively. The hysteresis was less than 3% relative humidity for the studied sensors. The response and recovery times depend on alternating current frequency and film composition and thickness of the studied polymers; the best response and recovery times were obtained for the thinnest film of PSDA-b-PEG as 2 and 3 minutes, respectively, at 100 kHz.

15) Yang Li et al [114] studied a novel humidity sensor composed of a 433 MHz surface acoustic wave (SAW) resonator and an interdigitated gold electrode connected in series. The gold electrode was covered with a sensitive film of a composite of processable conductive polyaniline and polyvinyl alcohol. The frequency response of the novel SAW-impedance humidity sensor toward relative humidity (RH) was investigated at room temperature. The
sensitivity of the SAW-impedance humidity sensors increased with the increase in the conductivity of the sensitive film. The sensor showed a sensitivity of $\sim 7.4$ kHz/%RH at 30%RH, which was increased to 60 kHz/%RH at 47%RH. Moreover, such sensors exhibited short response and recovery times and good repeatability. It is worth noting that the sensor showed a linear frequency response to humidity over the range of 0.4–20%RH with a good sensitivity of $\sim 2$ kHz/%RH, which reveals its potentials for detecting low humidity.

16) Fan-Wu Zenga et al [115] reported the Humidity sensor based on polyaniline nanofibres was fabricated and its response to humidity was investigated. It was found that the sensor behaved differently compared to commonly known conducting polymer based sensors. The sensor responded to low relative humidity (<50% RH) normally by decreasing electrical resistance with increasing humidity. However, at higher RH the sensor reversed its responses by increasing the electrical resistance with humidity. It is believed that the unique structure of nanofibres, which is more susceptible to distortion during polymer swelling, is responsible for the ‘reversed behaviour’. IR data confirmed that excess water absorption occurred and that a change in polymer oxidation state might also have taken place.

17) Patil P et al [116] reported the PANI-BaTiO$_3$ composites show better sensing properties than pure PANI, such as higher response factor and quicker response. The composites with 50 wt% of BaTiO$_3$ exhibit an exponential relationship between the resistance and RH irrespective of electrolyte pH used for the synthesis.

18) Fuke MV et al [117] reported that Spin coated films of Co-Polyaniline nanocomposite are evaluated for their transmission properties using He–Ne laser for humidity sensing. The samples exhibit typically two to three regions in their sensitivity curve when tested in the relative
humidity (RH) range of 20–95%. The sensitivity ranges from 0.1 mV / % RH to 12.26 mV / % RH for lower to higher thickness. The sensors show quick response of 8 s (20–95%RH), and a recovery time of 1 min (95–20%RH) with good repeatability, reproducibility and low hysteresis effect. The sensitivity of the sensor increases with humidity and thickness.

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