CONDUCTING POLYANILINE AND ITS NANOCOMPOSITES: INTRODUCTION, MATERIALS AND METHODS

Polymer systems with special properties are a field of increasing scientific and technical interest, offering the opportunity to polymer and synthetic organic chemists to synthesize a broad variety of promising new material, with a wide range of electrical and magnetic properties. Technological uses depend crucially in the reproducible control of the molecular and supramolecular architecture of the macromolecule via a simple methodology. Polyaniline is one such polymer whose synthesis does not require any special equipment or precaution. The formation of Polyaniline/montmorillonite nanocomposites with outstanding physical properties has considerable research attention due to its wide applications. In this chapter a general introduction to polyaniline and its clay nanocomposites are given revealing their importance in industry. The preparation conditions and various characterization techniques adopted for polyaniline/montmorillonite nanocomposites are also described.
10.0 INTRODUCTION

Polyaniline (PANI) is the typical phenylene based polymer having a chemically flexible -NH- group in the polymer chain flanked either side by a phenylene ring. The protonation, deprotonation and various other physico-chemical properties of PANI is due to the presence of the -NH- group\(^1\). It is the oxidative polymeric product of aniline under acidic conditions and has been known since 1862 as aniline black. At the beginning of the 20\(^{th}\) century organic chemists began investigating the constitution of aniline black and its intermediate products. Willstatter et al.\(^2,3\) in 1907 and 1909 regarded aniline black as an eight nuclei chain compound having an indamine structure.

During those periods it did not occur to anyone to investigate its electrical and magnetic properties for the obvious reason that organic compounds are insulators though in 1911 Mecoy and Moore suggested electrical conduction in organic solids\(^4\). Almost 50 years later Survile et al\(^5\) in 1968 reported proton exchange and redox properties with the influence of water on the conductivity of PANI. It was reported in 1973 that conductivity of inorganic polymer poly sulphur nitride (SN)\(_x\) is of the order of 10\(^3\) Scm\(^{-1}\) to be comparable with 6x10\(^5\) Scm\(^{-1}\) for Cu and 10\(^{14}\) Scm\(^{-1}\) for polyethylene. However, interest in PANI was generated only after the fundamental discovery in 1977 that iodine doped polyacetylene has a metallic conductivity\(^6\), which triggered research interest in new organic materials in the hope that these would provide new and improved electrical, magnetic, optical material or devices. The hope was based on electronic structure and the combination of the
metal like or semiconducting conductivity with the processability and flexibility of classical polymers and above all, the ease with structural modification can be carried out via synthetic organic chemical methodologies.

A significant breakthrough occurred in 1979 by the discovery that poly(para-phenylene) could be doped to conducting levels quite comparable to those in polyacetylene\textsuperscript{7-9}. This polymer is the first example of a non-acetylenic hydrocarbon polymer that can be doped with electron acceptors or electron donors to give polymers with metallic properties. This lead to the development of a new family of polymers, which with appropriate structural modifications can display conductivity from poor semiconductors comparable with that of copper.

The basic requirements of an organic material to become electrically conductive\textsuperscript{10} are that the component molecules or basic repeat units must be arranged in close proximity with overlapping orbitals with large extension perpendicular to the plane of the molecule. They must possess electron withdrawing substituents or highly polarizable side groups attached to the chain. The arranged units must be in crystallographically similar environments. This condition implies that the location of electrons is forestalled. Most general feature for efficient charge transport in organic systems is the existence of equally spaced atoms or groups not all in the same oxidation state. Migrations of positive charges occur from one end of the molecule to the other. Such a system will be metallic if it were infinitely long.
There are two types of electrical conductors, ionic and electronic. Ionic conduction in polymers is associated with polyelectrolyte, whereas electronic conduction is associated with \( \pi \)-conjugated polymers and is a relatively new phenomenon.

**10.1 CONDUCTION MECHANISM IN CONJUGATED POLYMER**

The reduction or oxidation process consists of adding or removing one electron to or from polymer chain, which causes the injection of states from the top of the valence band and bottom of the conduction band into the energy gap. This electronic excitation in polymeric material is accompanied by a distortion or relaxation of the lattice around the excitation, which minimizes the local lattice strain energy. The combined structural and electronic excitation will now look like a defect on the chain. From a chemical viewpoint, this defect is interpreted as a radical cation or radical anion, whereas physicists refer to it as a polaron which carriers both spin (1/2) and unit charge.

Removal or addition of a second electron from or to a polaron results in the formation of a bipolaron. A bipolaron is thus identified as a dication or dianion associated with a strong lattice site distortion, i.e. a bipolaron consists of two coupled polarons with charge equal to \( 2e^- \) and zero spin. The energy increase due to the coulombic repulsion (in the formation of a bipolaron) is compensated by the energy gained when the two charges share the same lattice distortion. Quantum chemical calculations indicate that the formation of bipolaron requires 0.4 eV less energy than the formation of two polarons.
Bipolarons must be formed by the coupling of pre existing polarons or possibly by the addition of charge to pre-existing polaron.

Scheme 10.1.1 Formation of charge carriers in conjugated polymer

In the case of polymers with degenerate ground state as in the case of polyacetylene, the charges can migrate apart to form solitons, i.e. two energetically equal structures at a point where they couple give a surface effect known as kink or a soliton. Soliton means 'solitary wave', implying a non-linear phenomenon involving non-dispersive transport of energy in a dispersive medium i.e. soliton has a movement. In a conjugated system soliton may be neutral, positively or negatively charged according to the number of electrons in the π-orbital. The separation of the charges is possible because a polyene
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segment of equivalent energy is formed between the charges as they separate. The formation of polaron, bipolaron and soliton is represented in scheme 10.1.1.

10.2 POLYANILINE (PANI)

The interesting variety of electronic structures that distinguishes PANI from other common conducting polymers was known from an early study by Green and Woodhead. Among all conducting polymers PANI has a special representation due to its easy synthesis, environmental stability, simple non-redox doping by protonic acids etc.

PANIs can be considered as being derived from a polymer, the base form of which has the generalized composition

![Chemical structure](image)

As seen from the above structure it consists of reduced and oxidized repeating units. The average oxidation state (1-y) can be varied continuously from zero, the completely reduced leucoemeraldine
Chapter 10

To half, the 'half oxidized' polymer emeraldine
to one, the completely oxidized polymer pernigraniline.

MacDiarmid et al.\textsuperscript{12} described five oxidation states and colours of PANI as: fully reduced or leucoemeraldine, protoemeraldine, emeraldine, nigraniline and pernigraniline. Protoemeraldine and emeraldine are conducting forms in the protonated state.
10.3 SYNTHESIS OF PANI

Chemical methods\(^{13}\) (figure 10.3.1) are widely employed for the synthesis of soluble and processable conducting polymers, electrochemical pathways are also used in several cases, and photochemical method is also known.

The simple polymerization process can be represented as

\[
\begin{align*}
\text{Ar-NH}_2 & \xrightarrow{\text{Ar-NH}_2} \text{Ar-NH-Ar-NH}_2 \\
\text{Ar-NH-Ar-NH-Ar-NH}_2 & \xrightarrow{2\text{e}^-, 2\text{H}} \text{Polyaniline}
\end{align*}
\]

The most preferred method for synthesis is to use either HCl or H\(_2\)SO\(_4\) with (NH\(_4\))\(_2\)S\(_2\)O\(_8\) as an oxidant\(^{14-17}\). Oxidative polymerization is a two electron change reaction and hence, the persulphate requirement is one mole per mole of a monomer. However, the smaller quantity of oxidant is used to avoid oxidative degradation of the polymer formed.

Several reports are there on the electrochemical synthesis of PANI\(^{18}\). Electrochemical polymerization is carried out by dissolving 0.1 mole of aniline in 1 mole protonic acid in distilled water at the platinum electrode by
Figure 10.3.1 Flowchart for chemical synthesis of PANI

Aniline salt of protonic acid + protonic acid

Mixed with stirring 0-5°C, 2 h

Filtered (ppt. collected)
Washed with distilled water, methanol/acetone

Dried under dynamic vacuum, 60-80°C, 8 h
EMERALDINE SALT

Treated with 0.1 M NH₄OH 6 h, PH ~9

Filtered, ppt. collected
Washed with distilled water, methanol/acetone

Precipitate dried under dynamic vacuum, 60-80°C, 8 h

EMERALDINE BASE
galvanostatic, potentiostatic or potentiodynamic methods as adopting the following conditions. Mechanism of PANI formation is shown in scheme 10.3.1.

Scheme 10.3.1 Mechanism of electrochemical polymerization of aniline
1. Galvanostatic \( \rightarrow \) constant current – Cd 1-10 mA during electrolysis

2. Potentiostatic \( \rightarrow \) Keeping potential constant

3. Sweeping the potential \( \rightarrow \) Between two potential limits - 0.2 to +1.0 vs SC

Electro polymerization appears to be a very straight-forward synthesis, but for a proper understanding of the phenomenon attention should be paid to the metal electrode/solution interface. Electrode materials normally used are transition and noble metals, whose electronic properties are governed by stronger localization of the d and f atomic orbitals, and the electronic work function of a metal plays an important role.

10.4 DOPING

The concept of doping is the unique, central, underlying and unifying themes, which distinguishes conducting polymers from all other types of polymers. The controlled addition of known, usually small (\( \leq 10\% \)) non-stoichiometric quantities of chemical species results in dramatic changes in the electronic, electrical, magnetic, optical and structural properties of the polymer. Doping is reversible to produce the original polymer with little or no degradation of the polymer backbone.\(^{20,21}\)
Table 10.4.1 Conductivity of electronic polymers

<table>
<thead>
<tr>
<th>Conductivity (Scm(^{-1}))</th>
<th>Conductivity (Scm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metals</strong></td>
<td></td>
</tr>
<tr>
<td>Ag, Cu</td>
<td>(10^{8})</td>
</tr>
<tr>
<td>Mg</td>
<td>(10^{4})</td>
</tr>
<tr>
<td><strong>Semi-conductors</strong></td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>(10^{-2})</td>
</tr>
<tr>
<td><strong>Insulators</strong></td>
<td></td>
</tr>
<tr>
<td>Nylon</td>
<td>(10^{-10})</td>
</tr>
<tr>
<td>Quartz</td>
<td>(10^{-16})</td>
</tr>
<tr>
<td>Doped trans (CH)(_x)</td>
<td>(10^{3})</td>
</tr>
<tr>
<td>Doped PANI</td>
<td></td>
</tr>
<tr>
<td>Trans (-CH-)(_x)</td>
<td>(10^{-3})</td>
</tr>
</tbody>
</table>

Conductivity increases with doping as seen from table 10.4.1. By controllably adjusting the doping level, conductivity anywhere that of the non-doped and that of the fully doped form of the polymer can be easily obtained. Conducting blends of a (doped) conducting polymer with a conventional polymer (insulator), whose conductivity can be adjusted by varying the relative properties of each polymer, can be made. This permits the optimization of the best properties of each type of polymer. PANI provides the prototypical example of a chemically distinct doping mechanism\(^{22}\).

Protonation by acid-base chemistry leads to an internal redox reaction and the conversion from semiconductor (emeraldine base) to metal (the emeraldine salt) (scheme 10.4.1). The chemical structure of the semiconductor...
emeraldine base form of PANI is that of an alternating copolymer. Upon protonation of the emeraldine base to the emeraldine salt, the proton induced spin-unpairing mechanism leads to a structural change with one unpaired spin per repeating unit, but with no change in the number of electrons.

Scheme 10.4.1 Internal redox reactions leading to the formation of polaron and bipolaron as a function of dopant
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The result is a half filled band and potentially, a metallic state where there is a positive charge in each repeating unit (from protonation) and an associated counter ion such as Cl, HSO₄, dodecyl benzene sulfonate etc.

PANI on doping to emeraldine salt form, undergoes an insulator to metal transition with a concomitant conformational change in the polymer backbone to accommodate this electronic transition. Zheng et al.²³ have suggested that this conformational change from compact coil to expanded coil is initiated by a proton doping mechanism, which generates (without loss of electrons) charge carriers along the backbone. The columbic repulsion of these polarons forces the polymer chain to adopt a more planar conformation. The result of this conformational change is a reduction of structural defects along the PANI chain, which increases the π-orbital overlap between the phenyl π-electron and nitrogen p-electrons. This, in turn increases both conjugation of the chain backbone and the polaron delocalization length. However, due to this conformational change, and greater polarity of the ionomeric form, the solubility of salt form is markedly reduced in dimethyl sulfoxide (DMSO) and N-methyl pyrrolidone (NMP) solvents compared to PANI base. This has resulted in PANI being often categorized as an intractable polymer. Recently, several methods has been reported to dissolve and process PANI in NMP, selected amines, conc. H₂SO₄ and other strong organic acids.

The melt and solution processability of PANI can be increased by protonation of PANI with a functionalized protonic acid. A functionalized protonic acid is generally denoted as H¹(M⁻-R), where H¹M⁻ is the protonic
acid group which may be sulphonic acid, carboxylic acid, phosphonic acid, sulphate or phosphate etc and R is an organic group. The proton of the protonic acid reacts with imine nitrogens of PANI and convert the base form to the conducting salt form; the (M'-R) group which serves as the counter ion. The R functional group is chosen to be compatible with non-polar or weakly polar organic solvents (e.g. dodecyl benzene sulphonic acid and camphor sulphonic acid). The organic substituted groups lead to solubility in common solvents such as toluene, xylene, chloroform etc and to compatibility with bulk polymers with similar molecular structure. The functionalized counter ions act as surfactants that enable intimate mixing of PANI in a variety of bulk polymers. PANI can be made soluble by substituting one or more hydrogens by alkyl, alkoxy, aryl, hydroxyl, amino or halogen groups in an aniline nucleus.

10.5 PANI – MONTMORILLONITE NANOCOMPOSITES

With the advent of newer and newer technologies, the demand for materials possessing a combination of a wide range of desirable properties is increasing day by day. One of the techniques to develop such materials is the formulation of composites from compatible materials individually possessing the desirable properties. In view of light weight, low cost, low temperature fabrication as well as mechanical strength and environmental stability, electrically conducting polymer, PANI with inorganic materials to form composites are important. Thus conducting polymers such as PANI have
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attracted great attention from researchers engaged in the research and development of new materials for various areas of modern engineering\textsuperscript{24}.

The introduction of an organic guest into an inorganic host material by the intercalation technique has resulted in the fabrication of nanocomposite materials with high potential for advanced applications\textsuperscript{25}. These nanocomposites consist of multilayered sandwich-like elements in which polymer chains are sandwiched between ultrathin sheets of an inorganic particle\textsuperscript{26}. Such confinement of polymer molecule is expected to lead to a high degree of polymer ordering and enhanced thermal and oxidative stability which is hard to find in pristine polymers.

It is important to note that many fundamental applications have become possible due to the use of nanoscale structural models for conducting polymers. Nanocomposites based on conducting polymer\textsuperscript{27} and different inorganic compounds are the representatives of the further development of ideas about nanostructuring, because such nanocomposites display novel and frequently important mechanical, electronic, magnetic, optical and catalytic properties inaccessible to both individual components of the nanocomposites and their micro analogues\textsuperscript{28,29}. The applications of polymer and inorganic materials includes as flame retardant, selective gas permeability\textsuperscript{30,31} and other synergistic properties that cannot be attained from individual materials\textsuperscript{32,33}.

Bein et al.\textsuperscript{34,35} demonstrated that encapsulation of PANI in a three dimensional host lattice (i.e. zeolites) and also reported the preparation of
conducting PANI filaments in a channel of mesoporous host MCM-41. This represents an important step towards the design and understanding of well defined conducting structures for nanometer scale electronic devices. Of the many possible organic guest/inorganic host combination available for study, the intercalation of PANI into layered compounds has received a great deal of attention and interest in the past decade. Many hybrid composites such as PANI/VOPO$_4$.2H$_2$O,$^{36}$ PANI/FeOCl$^{37}$, PANI/MoO$_3$$^{38}$, PANI/V$_2$O$_5$$^{39}$, PANI/graphite oxide$^{40}$, PANI/clay$^{41-46}$etc have been synthesized and studied. The combination of conducting polymer with host materials having different characteristics leads to new hybrid materials with novel properties and different conformation of polymer chains in the interlayer space may enable to further characterize the polymer structure.

Nano silicate layers leads to nanocomposites with important tensile strength and modulus, reduced gas permeability and decreased thermal expansion coefficient when compared with micro and macro composites counterparts and pure polymer matrix because of the high aspect ratio (width to thickness, 100~1000) of silicate layers and large surface area available for contact with the matrix polymer.

Clays among other hosts are natural, abundant and inexpensive mineral that have unique layered structure, high mechanical strength as well as high chemical resistance. Adoption of montmorillonite clay to the field of nanocomposites lies in its small particle size (<10 µm), ease of intercalation, easy hydration and capability to contain various organic/inorganic materials$^{47}$. 

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Their lamellar elements display high in-plane-strength, stiffness as well as high aspect ratio\textsuperscript{48}. Montmorillonite is the most abundant naturally occurring clay mineral.

Present study includes the preparation of PANI/montmorillonite composites and its characterization to know the nanocomposite structure. The confined, enhanced and non-expandable pillared clay (PILC) layers offer high polymer ordering within the matrix. The catalytic environment of montmorillonite allows efficient polymerization that allows high degree of polymer order and the restricted PILC matrix allows the formation of PANI nanofibers within the matrix.

The experimental procedure and characterization techniques used are discussed below. Next chapter discusses the results of nanocomposite fibers prepared over PILCs.

10.6 PREPARATION OF PANI/PILC NANOCOMPOSITES

The study of conducting polymers has become a major part of modern material science and in many institutes and commercial establishments involves multidisciplinary research into chemical synthesis, polymer preparation, electronics, physics and applied physics. The combination of metal-like or semiconducting conductivity and processability of classical polymers has created opportunities for scientists and technologies to investigate possible technological applications.
The most important characteristic of monomer molecules for the formation of conducting polymer is the requirement for the conversion of a closed shell system to a corresponding cation or anion radical and the stability of the product to form during the process. PANI is generally prepared by either chemical or electrochemical oxidation of aniline under acidic conditions. The control of the morphology of conducting polymers is a very stimulating challenge. The confined media polymerization of these conducting polymers is a very pertinent way to give them controlled shape and dimension.

PANI nanocomposites are prepared using PILCs as the inorganic host material.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>Merck</td>
</tr>
<tr>
<td>Ammonium peroxodisulfate</td>
<td>Qualigens</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>Qualigens</td>
</tr>
<tr>
<td>Ethanol</td>
<td>s.d.Fine chemicals</td>
</tr>
<tr>
<td>Acetone</td>
<td>s.d.Fine chemicals</td>
</tr>
<tr>
<td>Montmorillonite, KSF</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Na+-Exchanged Montmorillonite</td>
<td></td>
</tr>
<tr>
<td>PILCs</td>
<td></td>
</tr>
</tbody>
</table>

All materials are of high purity and used as it received

The nanocomposite is prepared by in-situ intercalative polymerization of aniline. The PILC is added to 1 M HCl aqueous solution and is stirred for 1
h. Aniline monomer is then added to this colloidal suspension of clay in a ratio of 50 mmol aniline/g clay, stirred for the intercalation of aniline into the silicate layers and is kept at 0°C. Ammonium persulfate, \((\text{NH}_4)_2\text{S}_2\text{O}_8\), dissolved in 1M HCl is added slowly to solution containing aniline and PILC at an aniline/oxidant molar ratio of 1:1.25, then stirred for 8 h and is kept overnight. The nanocomposite is separated by filtration and washing with acetone, methanol and distilled water. This is done to remove oligomers, excess oxidant and residual aniline monomer. The dark green PANI/Montmorillonite composite thus obtained is dried at 50°C. The washing for the removal of excess monomer and oligomers formed are done by extraction in a soxhlet apparatus.

The composites obtained are designated as PM, PNM, PXM and PXYM respectively when the clays are M, NM, XM (single PILCs) and XYM (mixed PILCs).

10.7 CHARACTERIZATION OF PANI/MONTMORILLONITE NANOCOMPOSITES

A thorough characterization of the composites are needed to know the extent of hybrid formation, structure of PANI within the layers, the polymer order, morphology, nature of charge carriers and stability of the polymer backbone within the layer. Here the different characterization techniques used and the results available are discussed. All instruments for the characterization studies are the same which is used in clay characterization.
10.7.1 FTIR ANALYSIS

PANI as described in 10.2 possess various structures among which emeraldine form is commonly found and promising with emeraldine salt possessing high conductivity. FTIR analysis reveals the chemical structure because the amount of energy (IR radiation) adsorbed is a function of the number of molecule present and provides both qualitative and quantitative information. In addition it gives an idea about the extent of oxidation and degree of protonation in the polymer chain. Infrared spectroscopy is a powerful tool to determine the structural changes that occur during doping. Various groups have reported FTIR results of PANI\(^{50-56}\). Generally, spectra of the composite show characteristic vibrations of both clay as well as the polymer. The peaks due to the benzenoid ring of PANI are present at around 1500 cm\(^{-1}\), 1512 cm\(^{-1}\), 1484 cm\(^{-1}\), 1289 cm\(^{-1}\), and 824 cm\(^{-1}\). Peaks at around 1581 cm\(^{-1}\), 1172 cm\(^{-1}\), and 800 cm\(^{-1}\) correspond to quinoid ring. The Si-O-Si stretching frequency of the clay matrix (~1050 cm\(^{-1}\)) present in the composite confirms the retention of basic clay structure\(^{57}\).

10.7.2 UV-VIS DRS ANALYSIS

The possible electronic transitions give an idea about the type charge carriers present in the PANI/montmorillonite nanocomposites. The diffuse reflectance spectra of PANI/montmorillonite shows peaks due to \(\pi-\pi^*\) (325-360 nm), polaron - \(\pi^*\) (400-430 nm) and \(\pi -\) polaron (780-826 nm) when PANI is in the doped state\(^{58,59}\).
10.7.3 XRD PATTERNS

XRD patterns of the PANI/Montmorillonite composites gives 2 types of observations. First one is the information about whether PANI is intercalated between the clay layers or not. In the case of montmorillonite as well as ion exchanged montmorillonite there is layer expansion as a result of polymer intercalation. This is found from the shift in $\theta$ value of $\sim 8.9^\circ$ in montmorillonite corresponds to the periodicity in the direction of (100) plane of the clay sample. Intercalation of PANI between the clay layers is evident from the shift of the peak towards left from Bragg equation. It is not possible in PILCs where appreciable layer expansion is already present but, the retention of the expanded layer structure may indicate that PANI polymers formed within the layers are in the order of nanometer range ($< 23 \, \text{Å}$).

The second information available from the XRD is about the crystallinity and thus the polymer order in the nanocomposite. High order leads to improved properties.

10.7.4 SEM ANALYSIS

The nanocomposite formation and the morphology of PANI within the matrix of clay layers are clearly seen from SEM pictures. Knowing the morphology allows the tuning of the composite to the required application.
10.7.5 TG/DTG ANALYSIS

The composite shows a four step weight loss in thermogravimetric analysis. The first weight loss just below 100°C is attributed to the loss of water from PANI as well as from the interlayer galleries of clay. The second weight loss ranging from 200 - 300°C is due to the elimination of dopant HCl present\textsuperscript{60}. The third weight loss is assigned to the thermal decomposition of PANI backbone chains\textsuperscript{61}. The weight loss around 620°C is attributed to the dehydroxylation of silicate structure. The polymer backbone breakage for pure PANI is at 530.6°C\textsuperscript{62}. In composite this is shifted to high temperature which may be due to the additional stability inside the matrix due to the restricted motion.

10.7.6 CONDUCTIVITY MEASUREMENTS

Conductivity is the reciprocal of specific resistance or resistivity, $\rho$. It can be designed as the conductance of 1 cm$^3$ of a material.

Conductivity = \( \frac{t}{a} \times \frac{1}{R} \) Scm$^{-1}$. where

- $t =$ thickness of the conductor
- $a =$ cross sectional area
- $R =$ resistance of the conductor

To determine the value of an electrical resistance of PANI composite, the dried samples were palletized and placed in between two electrodes which
were connected to a voltmeter. By applying a known current the resistance of the pellet was measured directly from the voltmeter.

\[ R = \frac{V}{I} \]

- **R** - Resistance
- **V** - voltage drop across the resistance due to current ‘I’ passing through the resistance.

Conductivity of pure emeraldine salt with HCl dopant lies in the order of \(10^{-2}-10^{-3}\). Composite formation with insulator clay will decrease the conductivity which lies in the order of \(10^{-1}-10^{-2}\). Anyway the conductivity can be tuned to a great extent to required level by varying the dopant concentration. The dc conductivity of PANI/clay composites at room temperature are measured through a linear four-probe Keithley resistivity set up.

### 10.8 CONCLUSIONS

- PANI is found to be one of the most important conducting polymers.
- Conductivity is due to the presence of conjugated double bonds, where delocalization is possible.

Composite formation is a widely used method for improving the properties and processability of polymers.
Clays, having a unique layer structure are important inorganic host material for the hybrid nanocomposite formation.

PANI/montmorillonite nanocomposites are prepared by using (NH₄)₂S₂O₈ as the initiator oxidant following the in-situ intercalation of the monomers within the layers and subsequent oxidative polymerization.

FTIR shows the structure of PANI inside the layers and the basic clay layer retention.

UV-Vis DRS Analysis shows the possible electronic transition over the PANI chain.

XRD patterns show the intercalation and the crystallinity of PANI within the layers.

The morphology of the nanocomposite formed is studied from SEM photographs.

TG/DTG shows the temperature of PANI backbone breakage in composites.
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2. Wilstatter, Moore, Ber. 40 (1907) 2669.


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