SYNTHESIS AND CHARACTERIZATION OF POLYINDOLE/NICKEL OXIDE NANOCOMPOSITES

Project report submitted to the University of Calicut in partial fulfillment of the requirements for the award of the degree of

MASTER OF SCIENCE

In

POLYMER CHEMISTRY

By

SAHLA.OP
(Reg.No-KVATMPC013)

Under the Supervision of
Dr.M.T.RAMESAN
Associate Professor
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
THENHIPALAM

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DEPARTMENT OF CHEMISTRY

UNIVERSITY OF CALICUT, THEHNIPALAM

CERTIFICATE

This is to certify that the project entitled "**SYNTHESIS AND CHARACTERIZATION OF POLYINDOLE/NICKEL OXIDE NANOCOMPOSITES"** is an authentic record of the project work done by **SAHLA.OP (KVATMPC013)** under my supervision and guidance in partial fulfillment of the requirement for the award of the Degree of M.Sc. Programme in Polymer Chemistry.

Calicut

June 2021

Dr. M. T. RAMESAN
(Associate Professor)

MES KEVEEYAM COLLEGE
VALANCHERY

P.O. Valanchery, Malappuram Dist, Kerala, Pin: 676 552.
Phone: 0494-2642670
www.meskvmcollege.org, Email: principal@meskvmcollege.org

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Prof.Rukkiya K.M
Head of the Department
Department of Chemistry
MES Keveeyam College
Valanchery

SYNTHESIS AND CHARACTERIZATION OF POLYINDOLE/NICKELOXIDE NANOCOMPOSITES

Submitted by

SAHLA.OP
(KVATMPC013)

The project presentation / viva voice held on ------------------------------ at MES Keveeyam College,Valanchery is evaluated and approved by

External Examiners:

DECLARATION

I hereby declare that the matter embodied in the dissertation entitled **"SYNTHESIS AND CHARACTERIZATION OF POLYINDOLE/NICKEL OXIDE NANOCOMPOSITES"** submitted to University of Calicut in partial fulfillment of the requirements for the award of the degree of M.Sc. Programme in Polymer Chemistry is the result of investigations carried out by me under the supervision of **Dr.M.T.RAMESAN**, Associate Professor, Department of Chemistry, University Of Calicut and the same has not been submitted elsewhere for a degree.

In keeping with the general practice of reporting scientific observation, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Place: Valanchery

Date: (SAHLA.OP)

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At all outset, I would like to kneel down before God Almighty for gave me strength, health and wisdom to complete this work successfully.

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My aknowledgement would be incomplete, if I did not express my gratefulness to my parents for their endless support, without which I could not complete my project work.

Finally, I state that I am alone responsible for the entire faults that remain in this project.

ABSTRACT

In the last few years conducting polymers have emerged with various diverse material properties thereby suiting for several applications such as supercapacitors,nano coatings , catalysis, biomedical, sensors etc..The fundamental characteristic of conducting polymer is the extended conjugated pi system within the polymer backbone ,which lead to metal like electronic, magnetic,optical properties,while properties commonly associated with conventional polymer such as flexibility are maintained.

The research area of conducting polymer is very challenging for researchers as the properties of the material are altered by minute changes in the synthetic condition.as most of the present nanofillers used to prepare nano composite are inorganic ,their processability ,biocompatibility,nano toxicity is much more limited than those of naturally organic ones.over the last few years much efforts has been devoted to the use of nano crystals obtained from polysaccharides as reinforcing agents in the polymer matrix .The advantage of natural fillers are their low density,renewable character,high specific strength and biodegradability associated withthe high specific properties of nanoparticles. The combination of a biocompatible material with conducting polymers offers a wide platformwith outstanding properties with advantageous functionality for bioelectronics and biosensors.this work is desired to examine the effect of nickel oxide nanoparticle in the polyindole conducting polymer.the goal of present work is to develop a polymer bio nano composite with enhanced thermal and electrical properties.

CONTENTS

CHAPTER 1

INTRODUCTION

1.INTRODUCTION

1.1 POLYMERS

Polymers form a very important class of materials without which life seems very difficult. They are all around us in everyday use; in rubber, in plastic, in resins, and adhesives and adhesives tapes. The word "polymer" means "many parts" (from the Greek poly, meaning "many," and mero, meaning "parts") and of high molecular mass each molecule of which consists of a very large number of single structural units joined together regularly. Polymers are giant molecules of high molecular weight, called macromolecules, which are build up by linking together a large number of small molecules, called monomers. The reaction by which the monomers combine to form a polymer is known as polymerization. Because of their wide range of properties, both synthetic and natural polymers play an essential role in everyday life. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. From 1811 Henri Braconnot did pioneering work in derivative cellulose compounds, perhaps the earliest important work in polymer science. The development of vulcanization later in the nineteenth century improved the durability of the natural polymer rubber, signifying the first popularized semi-synthetic polymer. In 1907 Leo Baekeland created the first completely synthetic polymer, Bakelite, by reacting phenol and formaldehyde at precisely controlled temperature and pressure. Most of the polymers around us are made up of a hydrocarbon backbone. A Hydrocarbon backbone being a long chain of linked carbon and hydrogen atoms, possibly due to the tetravalent nature of carbon. A few examples of a hydrocarbon backbone polymer are polypropylene, polybutylene, polystyrene. Also, there are polymers which instead of carbon have other elements in their backbone. For example, Nylon, which contains nitrogen atoms in the repeated unit backbone.

Molecules in a thermoplastic are held together by relatively weak intermolecular forces so that the material softens when exposed to heat and then returns to its original condition when cooled. Thermoplastic polymers can be repeatedly softened by heating and then solidified by cooling - a process similar to the repeated melting and cooling of metals. Most linear and slightly branched polymers are thermoplastic. All the major thermoplastics are produced by chain polymerization. e.g. polyethylene, polystyrene, polyindole. A thermosetting plastic, or thermoset, solidifies or "sets" irreversibly when heated. Thermosets cannot be reshaped by heating. Thermosets usually are three-dimensional networked polymers in which there is a high degree of cross-linking between polymer chains. The cross-linking restricts the motion of the chains and leads to a rigid material. Thermoset plastics offer an enhanced high-performance combination of thermal stability, chemical resistance, and structural integrity. Thermoset components are used extensively in a wide range of industries – and are used for applications in the automotive, appliance, electrical, lighting, and energy markets due to excellent chemical and thermal stability along with superior strength, hardness, and moldability. e. g polyester, polyamides, epoxy, silicone [1,2].

1.2 CONDUCTIVE POLYMERS

Polymers are insulating materials. For example; metallic cables are covered in plastic to shield them. However, there are four major classes of semiconducting polymers that have been developed so far which include conjugated conducting polymers, charge transfer polymers, ionically conducting polymers, and conductively filled polymers. The conductively filled polymers were first made in 1930 for the prevention of corona discharge. The invention of new substances with outstanding properties often leads to the latest technology.

Conductive polymers or, more precisely, **intrinsically conducting polymers (ICPs)** are organic polymers that conduct electricity. They are oligomeric or polymeric materials composed of phenylene rings and related units such as naphthalene, anthracene, or heteroaromatic rings such as pyrrole and thiophene, which are connected through carbon-carbon single bonds or through vinylene groups (-C=C-). These polymers have unique electrical and thermophysical properties. Due to the low hydrogen content and aromatic structure, they show excellent chemical, thermal, and oxidative stability and are practically insoluble in all common solvents. They are also potentially electrical conducting materials, particularly when doped. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. The electrical properties can be fine-tuned using the methods of organic synthesis and advanced dispersion techniques. These types of polymers have a solid backbone made up of an **extensively conjugated system**, which is responsible for conductance.

In the late 1970s, many scientists considered CPs (or ‘synthetic metals’) to be intractable and insoluble. Since the discovery of polyacetylene in 1977 by **Hideki Shirakawa, Alan MacDiarmid, and Alan Heeger**, various important CPs have been investigated continuously, including polypyrrole (PPy), polyaniline (PANI), polythiophene (PT), poly(3,4-ethylenedioxythiophene) (PEDOT), trans-polyacetylene, and poly (p-phenylene vinylene.

There are two main methods used to synthesize conductive polymers, chemical synthesis, and electro (co)polymerization. The chemical synthesis means connecting the carbon-carbon bond of monomers by placing the simple monomers under various conditions, such as heating, pressing, light exposure, and catalyst. The advantage is high yield. However, there are many impurities plausible in the end product. The electro (co)polymerization means inserting three electrodes (reference electrode, counter electrode, and working electrode) into the solution including reactors or monomers. By applying a voltage to electrodes, a redox reaction to synthesize polymer is promoted. Electro (co)polymerization can also be divided into Cyclic Voltammetry and Potentiostatic method by applying cyclic voltage and constant voltage. The advantage of Electro (co)polymerization is the high purity of products. But the method can only synthesize a few products at a time [3,4].

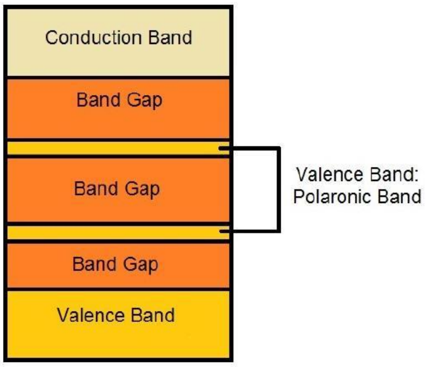
MECHANISM OF ELECTRICAL CONDUCTION IN CONDUCTIVE POLYMERS

Polymers are organic macromolecules, a long carbonic chain, composed of structural repeat entities, called *mer.* These smallest units, for instance, are bonded by covalent bonds, repeating successively along a chain. The majority of polymers are insulators, due to the unavailability of free electrons to create conductivity. In a covalent bond, the electrons are locked in these strong and directional bonds, so when an electric field is applied, electrons cannot drift. Therefore, these types of materials do not show a high conductivity. The poor conductivity of polymers is also explained by the band theory. This theory says that the energy levels of electrons can occupy are grouped in allowed bands and may have energy levels of the electron that are forbidden denominated bandgap. This theory results from Schrödinger’s Equation applied in a periodic field of a crystal solid. The lowest bands are called valence bands and are inert from an electrical perspective. On the other hand, the highest bands, which participate in electric conduction, are called conduction bands. Some conductors have a partially filled valence band that is relatively easier to excite an electron to a higher energy level. Other conductors, such as divalent metals can have an overlap of the empty conductive band with a filled valence band. For semiconductors and insulators respectively, the valence electrons must cross the bandgap to result in conduction. The difference is a semiconductor has relatively smaller bandgap energy than insulators have.

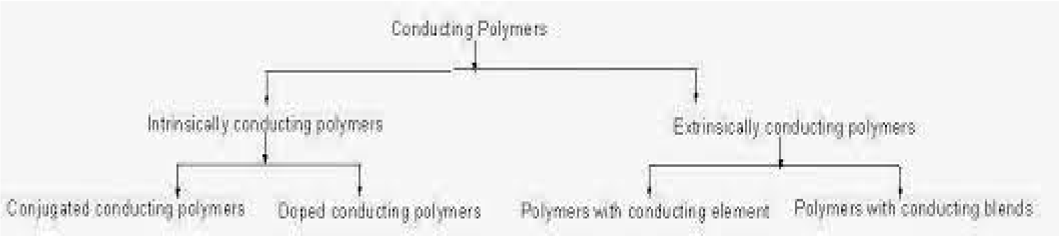
For a long period, polymers were considered insulators. Until, 1970, when the first intrinsic conductive polymer was produced by Shirakawa, Heeger, and MacDiarmid, which resulted in the Nobel prize in 2000. The polymer was produced by the exposure of the polyacetylene to dopant compounds: oxidizing or reducing agents; electron-donor or electron-receptor of electrons.

Conductive polymers are peculiar in that they conduct current without having a partially empty or partially filled band. Their electrical conductivity cannot be explained well by simple band theory. The mechanism of conduction and behavior of charge carriers in the conducting polymers have been explained using the concept of **polarons and bipolarons**. The process of doping conductive polymers becomes easier due to the conjugated bonds. In this process, defects and deformations in the polymeric chain are formed. An electron-deformation pair, or also an electron-phonon cloud pair, is called polarons, which are responsible for the conductivity in polymers. Bipolaron and solitons, other types of quasi-particles, also participates in the conductivity mechanism. The type of soliton, bipolaron or polaron formed depends on the dopant used. From the point of view on the binding energy, it is assumed that a band edge exists and that beyond this energy the holes/electrons are "free". At this energy range, the free carriers move in an un-correlated manner, meaning that the knowledge of the position of either an electron or hole does not yield any information about the location of the other. Any energy state that lies below the band edge is known as an excitonic state (or polaronic state if it is charged). In these states, the motion of the electrons is correlated, and the electrons (holes) are bound. The energy difference between the band edge and the excited state is the binding energy, and the fast excitation before the surrounding configuration could react is to an unbound state. The different excitations in the conjugated polymers differ in the charge they carry: A positive/negative Polaron is an excitation that carries a single positive/ negative electron charge. A Bipolaron is a double charged excitation. An exciton is a neutral excited state, which simplistically, can be described as carrying a dipole. A radical cation that is partially delocalized over some polymer segment is called a polaron. It stabilizes itself by polarizing the medium around it. It is a radical cation and has a spin of ½. When an electron is removed from the top of the valence band of a conjugated polymer, a vacancy (hole or radical cation) is created that does not delocalize completely, as would be expected from classical band theory. Only partial delocalization occurs, extending over several monomeric units and causing them to deform structurally. The energy level associated with this radical cation represents a destabilized bonding orbital and thus has higher energy than the energies in the valence band. This rise in energy is similar to the rise in energy that takes place after an electron is removed from a filling bonding molecular orbital. If another electron now is removed from the already oxidized polymer containing the polaron, two things can happen: This electron could come from either a different segment of the polymer chain, thus creating another independent polaron, or from the first polaron level (remove the unpaired electron) to create a special dication, which is called a bipolaron. Low doping levels rise to polarons, whereas higher doping levels produce bipolarons. Compared to the polaron, bipolaron is doubly charged but spins less. The bipolaron also has structural deformation associated with it. The two positive charges of the bipolaron are not independent but act as a pair. Both polarons and bipolarons are mobile and can move along the polymer chain by the rearrangement of double and single bonds in the conjugated system that occurs in an electric field. If many bipolarons are formed, say as a result of high doping, their energies can start overlapping at the edges, which creates narrow bipolaron bands in the bandgap.

The energy spacing between the highest occupied and the lowest bandgap. The highest occupied band is called the valence band, and the lowest unoccupied band is the conduction band. Conducting polymers either have a zero energy band gap or a very low bandgap. The optical band gap controls the electronic and optical properties of conducting polymers. A reduction in the optical band gap increases the conductivity of the polymers. So, attempts have been made to reduce the bandgap in conducting polymers by various methods. The bandgap of any of the well–studied conducting polymers is greater than 2.0 eV. The constant movement of the double bonds to stabilize the charge in the neighbor atoms causes, therefore, the movement of the charge, resulting in the conductivity. This movement of double bonds is called resonance and it describes the delocalized electrons within a molecule. A delocalized electron is an electron, presented in a π bond, which is shared by three or more atoms. Due to this process of the polaron formation, there is a change in the band structure of the conductive polymer. It creates the polaronic conduction bands, allowed bands in the bandgap, reducing the bandgap energy, making the polymer able to conduct, as shown in the figure.[5-7]



CLASSIFICATION OF CONDUCTING POLYMERS



INTRINSICALLY CONDUCTING POLYMERS

(i) **Conducting polymers having conjugated π-electrons in the backbone**: These polymers essentially contain a conjugated π-electron backbone responsible for electrical charge. Under the influence of the electrical field conjugated π -electrons of the polymer get excited, which can then be transported through the solid polymer [8]. Further, overlapping of orbitals of conjugated π -electrons over the entire backbone results in the formation of valence bands as well as conduction bands, which extend over the complete polymer molecule. The presence of conjugated π -electrons in polymers increases its conductivity, e.g., Polypyrrole.

(ii) **Doped conducting polymers**: The conducting polymers obtained by exposing the polymer to a charged transfer agent in either gas phase or solution are called doped conducting polymers. Doping is the process by which the conductivity of the polymers may be increased by creating a negative or positive charge on the polymer backbone by oxidation or reduction. Doping may be of two types [9]:

- **p-Doping**: The polymers which have conjugation in the backbone when treated with electron-deficient species like $FeCl_3$ or I_2 vapor. It is done by an oxidation process. Removal of one electron from the pi-back bone of a conjugated polymer forms a radical, called polaron which on losing another electron forms bipolaron. In this process, the conducting polymer is treated with Lewis acid.

  $(CH)_x + A \rightarrow (CH)^-_x\ A^+$

- **n-Doping**: When Lewis bases are treated with polymers having conjugation, due to the reduction of the polymer, a negative charge develops. By the addition of electrons, polaron and bipolaron are formed. It is done by the reduction process.

  $(CH)_x + B \rightarrow (CH)^-_x\ B^+$

Extrinsically conducting polymers: Those conducting polymers that owe their conductivity due to the presence of externally added ingredients in them are called extrinsically conducting polymers.

They are of two types:

(i) **Conductive element-filled polymers:** In this type, the polymer acts as a binder to hold the conducting elements together in a solid entity. The minimum concentration of the conductive filler, which is added to let the polymer start conducting is called the percolation threshold. Important characteristics of these polymers are, They possess good bulk conductivity, They are cheaper, light in weight, mechanically durable and strong, easily processable in different forms, shapes, and sizes.

(ii) **Blended conducting polymers**: These types of polymers are obtained by blending a conventional polymer with a conducting polymer either physically or chemically. Such polymers can be easily processed and possess better physical, chemical, and mechanical properties.

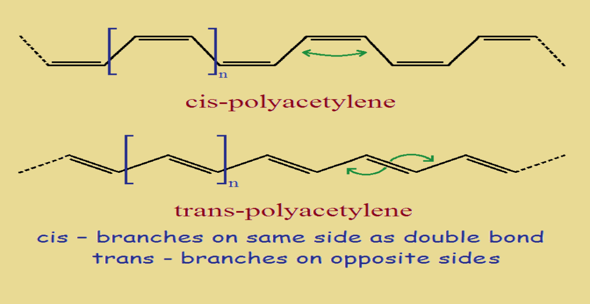
DOPING

In a conjugated system, the electrons are loosely bonded and an electron flow is possible. However, as the polymers are covalently bonded, the material needs to be doped for electron flow to occur. Doping is either the addition of electrons or the removal of electrons from the polymer. Once doping has occurred, the electrons in the π-bonds can “jump” around the polymer chain and, while electrons are moving along the molecule, an electrical current flows. CPs have been doped using different methods to achieve high conductivities. Un-doped polymers have been reported as insulators but, upon doping, their conductivity can change from insulating to metallic. Owing to their unique chemical structures, however, the doping mechanism for CPs is completely different from that for their inorganic counterparts. Dopants in the polymer undergo redox processes in which charges are transferred with the subsequent formation of charge carriers. The role of the dopant is not only to withdraw electrons from the CP but also to add electrons to the CP backbone. A simple explanation of the effect of doping is that electrons are extracted from the highest occupied molecular orbital (HOMO) of the valence band (oxidation) or transferred to the lowest unoccupied molecular orbital (LUMO) of the conduction band (reduction). This oxidation/reduction process creates charge carriers in the form of polarons (radical ions), bipolaron (dications or dianions), or solitons in the polymer. CPs can be categorized into degenerate and non-degenerate systems based on their bond structures in the ground state. Degenerate polymers possess two identical geometric structures in the ground state while non-degenerate polymers exhibit two different structures with different energies in the ground state (e.g., benzenoid and quinoid structures, where the energy of the benzenoid is lower than that of the quinoid). Solitons are known to be the charge carriers in degenerate systems such as polyacetylene [10-12]. Conversely, polarons and bipolarons serve as the charge carriers in both degenerate and non-degenerate systems such as PPy and PT. The movement of these charge carriers along polymer chains produces conductivity. In solid-state physics terminology, the oxidation and reduction processes correspond to p-type and n-type doping, respectively. In p-type doping, the electron moves directly from the HOMO of the polymer to the dopant species and creates a hole in the polymer backbone. Conversely, in n-type doping, electrons from the dopant species move to the LUMO of the polymer, resulting in increased electron density. Hence, the density and mobility of charge carriers can be tuned by doping. CPs can undergo both p-type doping and n-type doping, as shown in Figure 2. The doping process generates positive or negative polarons/bipolarons. These charge carriers are delocalized over the polymer chains, which facilitates electronic conductivity. Generally, the negatively charged carriers in n-doping are not as stable as positively charged forms, which makes p-doping more popular in academic research as well as for practical applications. Representatively, the conductivity in PPy is an outcome of p-type doping. In such compounds, the energy gap can be > 2 eV, which is too great for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophenes, polyacetylenes only have a low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. Even at a very low level of doping (< 1%), electrical conductivity increases several orders of magnitude up to values of around 0.1 S/cm. Subsequent doping of the conducting polymers will result in a saturation of the conductivity at values around 0.1–10 kS/cm for different polymers. The highest values reported up to now are for the conductivity of stretch-oriented polyacetylene with confirmed values of about 80 kS/cm.

1.3 DIFFERENT CONDUCTING POLYMERS

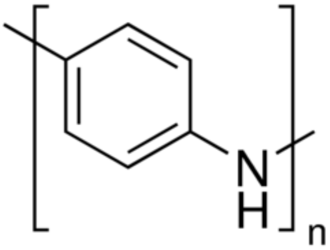
POLYACETYLENE

Polyacetylene or polyethylene (repeating unit C_2H_2) is a rigid, rod-like polymer that consists of long carbon chains with alternating single and double bonds between the carbon atoms. It is a well-known conductive polymer as its discovery started the development of (doped) highly conductive organic polymers. Its electrical conductivity was discovered by Hideki Shirakawa, Alan Heeger, and Alan MacDiarmid who received the Nobel Prize in Chemistry in 2000 for their work. They synthesized this polymer for the first time in the year 1974 when they prepared polyacetylene as a silvery film from acetylene, using a Ziegler-Natta catalyst. Despite its metallic appearance, the first attempt did not result in a conductive polymer. However, three years later, they discovered that oxidation with halogen vapor resulted in a conductive polyacetylene film, which had a much higher conductivity than any other previously known conductive polymer. Although its discovery started the development of conductive organic polymers, polyacetylene has no commercial applications [13].

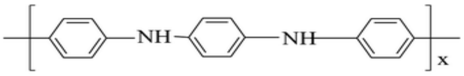


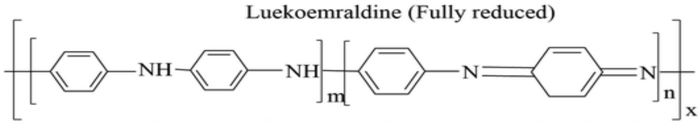
A variety of methods have been developed to synthesize polyacetylene, from pure acetylene and other monomers. One of the most common methods uses a Ziegler–Natta catalyst, such as Ti $(OiPr)_4/Al(C_2H_5)_3$, with gaseous acetylene. When polyacetylene films are exposed to vapors of electron-accepting compounds (p-type dopants), the electrical conductivity of the material increases by orders of magnitude over the undoped material. p-type dopants include Br_2, I_2, Cl_2, and AsF_5. These dopants act by abstracting an electron from the polymer chain. The conductivity of these polymers is believed to be a result of the creation of charge-transfer complexes between the polymer and halogen. Charge-transfer occurs from the polymer to the acceptor compound; the polyacetylene chain acts as a cation and the acceptor as an anion. The "hole" on the polymer backbone is weakly associated with the anionic acceptor by Coulomb potential. Polyacetylene doped with (p-type) dopants retain their high conductivity even after exposure to air for several days. Electron-donating (n-type) dopants can also be used to create conductive polyacetylene. n-Type dopants for polyacetylene include lithium, sodium, and potassium [14].

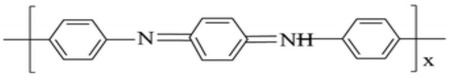
POLYANILINE



Conducting polymers have received ever-increasing attention, especially in the last two decades. Among them, polyaniline (PANI) is popular for its ease of preparation, good level of electrical conductivity, and environmental stability. It is prepared by the oxidative polymerization of aniline with a suitable oxidant, e.g., ammonium peroxydisulfate. The conductivity of polyaniline is dependent upon the dopant concentration, and it gives metal-like conductivity only when the pH is less than 3. Polyaniline exists in different forms. They are classified as leucoemeraldine, emeraldine, and pernigraniline, by their oxidation state, *i.e.*, leucoemeraldine exists in a sufficiently reduced state, and pernigraniline exists in a fully oxidized state. Polyaniline becomes conductive only when it is in a moderately oxidized state and acts as an insulator in a fully oxidized state.

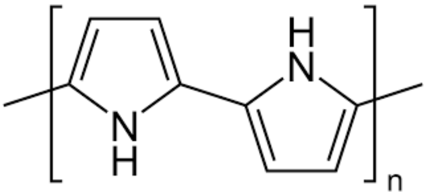

Luekoemraldine (Fully reduced)

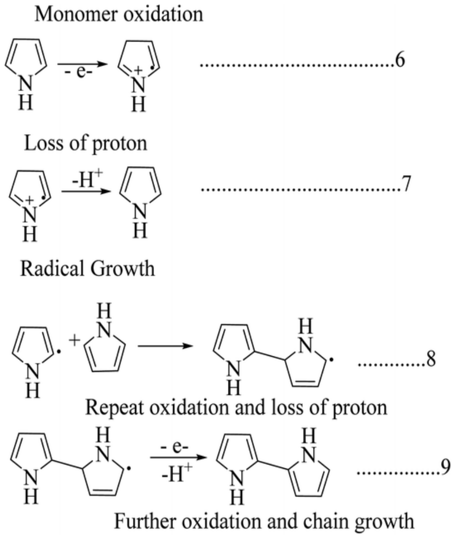

Emraldine (Partialy oxidized and Partially reduced)


Pernigraniline (Fully reduced)

The chemical oxidation method is one of the most straightforward methods to synthesize polyaniline; in this method, a monomer precursor of the corresponding polymer is mixed with an oxidizing agent in the presence of a suitable acid under ambient conditions to give products, where the doping acid and oxidizing agent are those preferred by the authors concerned. The change in color of the reaction medium to green indicates the formation of polyaniline. The preparation of the composite also follows the same method. Generally, oxidizing agents like ammonium persulfate, ammonium peroxy disulfate, ceric nitrate, ceric sulfate, potassium bichromate, *etc.* are used. Depending upon the pH of the acid dopant, the conductivity effectively modulates the physical parameters. The polymer and composite possess good conductivity when the pH is between 1 and 3. n doping with protonic acid (HA) two adjacent imine (=N-) groups of EB gets protonated and thus a bipolaron is formed. The bipolaron then rearranges to form polarons in which the positive charges are delocalized along the polymeric backbone. These positive charges are mobile and hence are responsible for conductivity. The major applications are printed circuit board manufacturing: final finishes, used in millions of m^2 every year, antistatic and ESD coatings, and corrosion protection [15-17].

POLYPYRROLE





Polypyrrole is unique due to its increased commercial interest because of its high stability, enhanced conductivity, and it is relatively easy to form homopolymer and composites from it. Polypyrrole was first prepared by the chemical oxidation of a pyrrole monomer in the presence of hydrogen peroxide, and it is black powdery material. Some of the first examples of PPy were reported in 1919 by Angeli and Pieroni, who reported the formation of pyrrole blacks from pyrrole magnesium bromide. Polypyrrole behaves like an insulating material in its undoped virgin state, and it shows a constant conductivity of 10^{-5} sm^{-1} when doped with halogenic electron acceptors such as bromine or iodine. electrochemical synthesis is widely used to obtain highly conductive Polypyrrole, where the procedure and technique are similar to those of other conducting polymers. The yield of the product is limited in this technique due to the reduced anode size. The main advantage this method has over other techniques is that we can control the thickness and morphology by controlling the electrochemical parameters. Some factors affect the conductivity and yield:

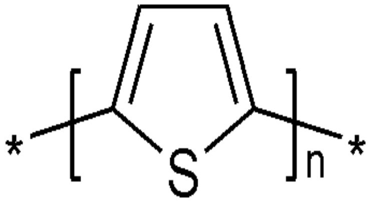
(1) solvent type and oxidant used;
(2) pyrrole/oxidant ratio;
(3) reaction temperature and reaction time.

When polypyrrole is prepared with a $FeCl_3$ oxidant, the final product is doped with Cl^- anions.

$$nC4H5N + (2 + y)\ nFeCl3 \rightarrow [(C4H3N)ny+ny\ Cl-]+ + (2 + y)nFeCl2 + 2n\ HCl$$

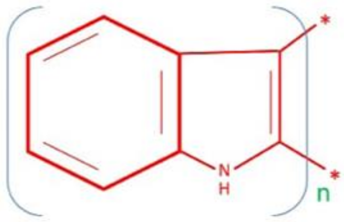
Generally conducting polymers are semiconductors with a filled valence band and empty conduction band. These bands are separated by an empty gap. Doping creates new bands in the energy gap, making it possible for the electrons to move to these new bands and increasing the conductivity of the materials. In the reduced (undoped) form PPy polymers are insulators. Bipolaron plays an important role in the transport and electronic properties of polymers. The charge carriers are the positive charges created on the polymer back born (commonly called polarons). PPy and related conductive polymers have two main applications in electronic devices and for chemical sensors [18].

POLYTHIOPHENE



Polythiophenes (PTs) are polymerized thiophenes, a sulfur heterocycle. The parent PT is an insoluble colored solid with the formula $(C_4H_2S)_n$. The rings are linked through the 2- and 5-positions. Polythiophene and its derivatives are extensively studied for their environmental stability, thermal stability, less bandgap energy, and high optical property compared with other conducting polymers. Polythiophene was chemically synthesized in the early 1980s by the Yamamoto and Lin–Dudek routes. Other advanced techniques, like direct sol-gel, oxidative synthesis, organometallic coupling reaction, electropolymerization, template-assisted synthesis, and hydrothermal and solvothermal techniques, have been effectively studied. The electronic and optical properties of polythiophenes can be modulated by doping engineering or by chemical modifications. The bandgap of polythiophenes varies 3–1 eV depending on the dopant and side-chain employed. Upon treatment with oxidizing agents (electron-acceptors) however, the material takes on a dark color and becomes electrically conductive. Oxidation is referred to as "doping". Upon "p-doping", charged unit called a bipolaron is formed. The bipolaron moves as a unit along the polymer chain and is responsible for the macroscopically observed conductivity of the material. Poly(3,4-ethylenedioxythiophene) (PEDOT) is an important derivative of polythiophene and it was thoroughly studied for its high electrical and electro-optical properties. The main problem with the PEDOT derivative is its insolubility in water. This was successfully overcome by introducing polyelectrolyte-like polysulfonates (PSS) into the PEDOT matrix. PSS acts as both a dopant and a stabilizer by a charge balance mechanism. The PEDOT: PSS derivative has high conductivity, good mechanical flexibility, and long-term thermal stability [19]. Conductivity can approach 1000 S/cm.

POLYINDOLE



Polyindole

The leading applications of conducting polymers are focus on different areas, such as rechargeable batteries, fabrication of electronic devices, solar energy conversion, sensors, electromagnetic shield, molecular electronics. Besides this, the electroactive properties of heterocyclic conjugated conducting polymers containing nitrogen atoms such as polyaniline, polypyrrole, polycarbazole, and their derivatives have fascinated significant interest due to their potential applications in research and industrial fields. These heterocyclic conjugated conducting polymers have received a great deal of attention because of their good electrical properties, environmental stability, and ease of synthesis [20].

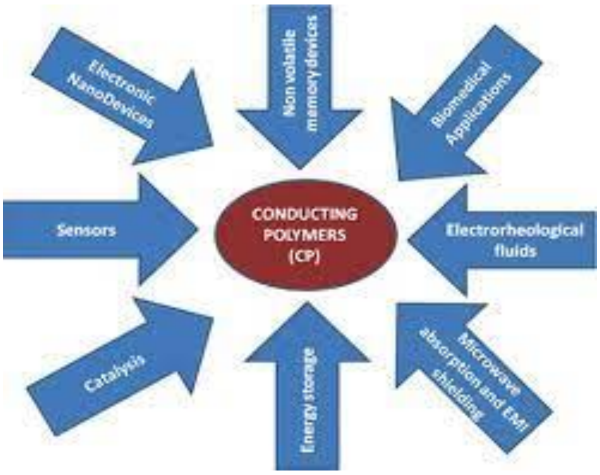
Among these heterocyclic conducting polymers, polyindole (PIn) possesses the properties of both poly(para-phenylene) and polypyrrole together, such as relatively high electrical conductivity, high thermal stability, slow degradation rate, and good-redox activity and stability. However, only a limited number of investigations have been carried out on chemically synthesized PINs. PIN possesses high electrical conductivity; however, it has poor thermal stability and processability and is insoluble, infusible, and brittle. The electroactive PIn is normally synthesized at room temperature through chemical approaches: emulsion polymerization; interfacial polymerization; electrochemical polymerization and chemical polymerization of indole monomer. The oxidative couplings of indole can be obtained by chemical polymerization technique with oxidants like $FeCl_3$ and $CuCl_2$.A polyindole (PIN) conducting polymer composite was chemically synthesized using $FeCl_3$ as an oxidizing agent in chloroform solution and nitrogen atmosphere at 10 °C. The polymerization efficiency and the conductivity of polyindole are lower than the other known hetero atom containing conducting polymers such as polycarbazole, polyfuran, polyisothianapthene, polythiophene, etc. Therefore, they did not attract much attention as the other types of conducting material [21-24].

APPLICATIONS OF CONDUCTING POLYMERS

- Conducting polymers are useful in discharging large quantities of static electricity in computer industries and chemical industries. This can be accomplished by coating the conducting polymer over an insulating surface. Hence conducting polymers are used as antistatic.
- ***POLYMER RECHARGEABLE BATTERIES:*** Repeated oxidation and reduction of polymer backbone constitute the principle of polymer rechargeable batteries. For example, polypyrrole lithium cell is a useful rechargeable battery compared to conventional Ni-Cd cell. So, these are environmentally safe and nontoxic
- ***POLYMER SOLAR CELL***: Polymer solar cells have attracted broad research interest because of their advantageous solution processing capability and the formation of low-cost, flexible, and large-area electronic devices.

- ***CHEMICAL SENSORS:*** Conducting, such as polypyrrole, polyaniline, polythiophene, and their derivatives, have been used as the active layers of gas sensors. There is two main application for the conducting organic polymers in electronics. The first one is that a polymer can be used as a **material for constructing different devices** and as **discriminating layers in electronic chemical sensors**

- ***CHEMIRESISTORS:*** The most widespread group of sensors is those that use conducting polymers. They are cheap and quite easily made up. In addition, they utilize the main property conductivity of conducting polymers. At its basic, a chemiresistor is simply formed by two electrodes as contact points with the conducting polymers put onto an insulating substrate.
- ***CORROSION INHIBITORS:*** Conducting polymers of various forms will be electrodeposited onto oxidisable metals and electrochemical and environmental means will be used to access their applicably for corrosion protection. PANI and its derivatives are used for corrosion protection. The electroactive coatings of PANI could provide adequate protection against corrosion of stainless steel and iron sheets, respectively.



1.4 POLYMER NANOCOMPOSITE

A composite material is a combination of two materials with different physical and chemical properties and distinguishable interfaces. polymer nanocomposite is a composite material comprising a polymer matrix and an inorganic dispersive phase that has at least one dimension that is nanometric in scale. Nanocomposites refer to composites in which one phase has nanoscale morphology such as nanoparticles, nanotubes, or lamellar nanostructure. The component materials don't completely blend or lose their identities; they combine and contribute their most useful traits to improve the outcome or final product. Composites are typically designed with a particular use in mind, such as added strength, efficiency, or durability. Additionally, as dimensions reach the nanometre level, interactions at interfaces of phases become largely improved, and this is important to enhance materials properties. In this context, the surface area/volume ratio of reinforcement materials employed in the preparation of nanocomposites is crucial to the understanding of their structure-property relationships. Further, the discovery of CNTs [25] and their subsequent use to fabricate composites exhibiting some of the unique CNT-related mechanical, thermal, and electrical properties [26] added a new and interesting dimension to this area. Almost all types of polymers, such as thermoplastics, thermosets, and elastomers have been used to make polymer nanocomposites. A range of nano reinforcements with different shapes has been used in making polymer nanocomposites. An important parameter for characterizing the effectiveness of reinforcement is the ratio of surface area (A) of reinforcement to the volume of reinforcement.

Polymer nanocomposites are **synthesized** via various methods that can be categorized into four major routes: **melt intercalation, template synthesis, exfoliation adsorption, and in situ polymerization intercalation**

- **Melt intercalation**

Melt intercalation is the typical standard approach for synthesizing thermoplastic polymer nanocomposites. It involves annealing the polymer matrix at high temperatures, adding the filler, and finally kneading the composite to achieve uniform distribution, as illustrated in Figure 1.2. It has the advantage of being environmentally friendly because of the lack of solvent usage. In addition, it is considered compatible with industrial processes such as injection moulding and extrusion, which makes it more convenient to utilize and, thus, more economical. However, the high temperatures used in the process can damage the surface modification of the filler.

- **Exfoliation Adsorption**

Exfoliation adsorption, also called polymer or prepolymer intercalation from solution, is based on a solvent in which the polymer or prepolymer is soluble. The layered silicate, for instance, is first swollen and dispersed in a solvent before mixing it with the polymer solution. The polymer chains then intercalate and displace the solvent within the silicate interlayers. Eventually, on the removal of the solvent, a multilayer structure is formed as the sheets reassemble trapping the polymer chains. This approach is widely used for water-soluble polymers to produce intercalated nanocomposites based on polymers with low or no polarity such as poly (vinyl alcohol), poly (ethylene oxide), poly (vinylpyrrolidone), or poly (acrylic acid). However, unlike melt intercalation, this method is environmentally unfriendly because of the usage of large amounts of solvents [27].

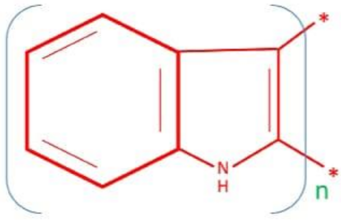
- **Template synthesis**

Template synthesis, also known as sol-gel technology, is based on an opposite principle to the previous methods. This approach involves the formation of the inorganic filler in an aqueous solution or gel containing the polymer and the filler building blocks. The polymer serves as a nucleating agent and promotes the growth of the inorganic filler crystals. As those crystals grow, the polymer is trapped within the layers and thus forms the nanocomposite. It is mainly used for the synthesis of double-layer hydroxide-based nanocomposite and is much less developed for the synthesis of layered silicates. This is because of the high temperature used during synthesis that degrades the polymer and the resulting aggregation tendency of the growing inorganic crystals. Therefore, this process is not commonly used [28].

➢ *IN-SITU POLYMERISATION*

In polymer chemistry, ***in situ polymerization*** is a preparation method that occurs "in the polymerization mixture" and is used to develop polymer nanocomposites from nanoparticles. The *in-situ* polymerization process consists of an initial step followed by a series of polymerization steps, which results in the formation of a hybrid between polymer molecules and nanoparticles. In situ polymerization involves the swelling of the filler in the liquid monomer or monomer solution as the low-molecular-weight monomer seeps in between the interlayers causing the swelling [30]. Polymerization starts either using heat, radiation, initiator diffusion, or by organic initiator or catalyst fixed through the cationic exchange. The monomers then polymerize in between the interlayers forming intercalated or exfoliated nanocomposites. The advantage of this approach lies in the better exfoliation achieved compared to melt and exfoliation adsorption methods. Several advantages are attributed to in situ polymerization. First of all, thermoplastic- and thermoset-based nanocomposites can be synthesized via this route. In addition, it permits the grafting of polymers on filler surfaces, which can generally improve the properties of the final composite. Partially exfoliated structures can be attainable with this method because of the good dispersion and intercalation of fillers in the polymer matrix. There are several advantages of the *in-situ* polymerization process, which include the use of cost-effective materials, being easy to automate, and the ability to integrate with much other heating and curing methods. Some downsides of this preparation method, however, include limited availability of usable materials, a short period to execute the polymerization process, and expensive equipment is required [31].

1.5 POLY INDOLE



Polyindole

Conjugated polymers are well-known for their excellent electrical conductivities in an oxidized (doped) state. The recent development of processable conducting polymers has opened the way for large-scale industrial applications. Heteroaromatic molecules containing nitrogen have very interesting properties. Polyindole (PIN) has received significant attention in the past several years. Indole has both benzene and pyrrole rings, so PIN may have the properties of both poly (para phenylene) and polypyrrole. The advantage of polyindole is the high redox activity, good thermal stability, and slow degradation rate in comparison with those of polyaniline and polypyrrole.

Polyindole (PIN) is an electroactive polymer, which can be obtained from electrochemical oxidation of indole or chemical oxidation using $FeCl3$ or $CuCl2$. However, only little investigations have been made on chemically synthesized polyindole. The PIN can be generated via numerous ways viz. Chemical oxidative polymerization, Electrochemical polymerization, Interfacial/Emulsion polymerization, etc. The second and third positions in the Indole ring are the sites for coupling where no involvement of the N atom and benzene is observed during polymerization. The effect of substitution on Indole ring and the choice of solvent used in various methods of syntheses play a significant role in the overall polymerization of the monomer

Chemical oxidative polymerization: For fabrication of polymer via chemical oxidative method there is a requirement of monomer along with a suitable oxidising and doping agent. Though various studies suggest the use of various oxidants $FeC1_3$, H_2O_2, APS, $CuCl2$, etc are the most commonly used ones. Also, the use of certain solvents viz. ethanol, methanol, ethanol-water, water, phenol, etc. are used to make the effective medium of monomer, oxidant, surfactant (SDS, CTAB, SLS, TW-80, etc.), and dopant (most commonly acidic). The nature of oxidants, used solvent, applied temperature, the concentration of reagents strongly affects the polymerization. In recent years, Polyindole (PIN), is being explored and developed as a possible candidate for electrical energy storage. The PIN is the least studied CP studied for energy storage as compared to others certainly owing to its low electrical and electrochemical conductivity as compared to PPY and PANI by a factor of two. Likewise, other intensively used CP, PIN also suffer from disadvantages like instability, mechanical strain over long cycles, material degradation, and loss which, in a long time, can even lead to a loss in capacity and collapse of capacitor device. The PIN is a non-planar, light-weighted, loosely compact, and arbitrarily oriented polymer leading weak association among the polymer chains leading to low conductivity. The reason behind this mechanical instability and other disadvantage is maximally attributed to structure irregularity in their chain. To overcome the discussed loopholes, to make PIN technically feasible, and to enhance its performance certain modifications in the existing polymer are being carried on [32,33].

1.6 NICKEL OXIDE NANOPARTICLE

Nickel oxide is the chemical compound with the formula NiO. It is an important transition metal oxide with cubic lattice structure. The mineralogical form of nickel oxide is bunsenite which is very rare. Nickel oxide nanoparticle are white spherical high surface area metal particles. Nanoscale nickel oxide particles are typically 10-30 nanometers. Nano nickel oxide particles are also available in Ultra high purity, carbon coated, passivated and dispersed forms. Varying the particle size of NiO leads to novel and interesting magnetic properties. The dielectric use of NiO nanoparticles are high at low frequencies that decrease rapidly with the applied frequency at all temperatures. The high value of dielectric constant may be attributed due to the increased ion jump orientation effect exhibited by nanoparticles. Defects present in the structure of nickel oxide nanoparticle will lead to non-stoichiometric nickel oxide which is a good p-type semiconductor. Recently several methods have been used to prepare ultrafine nickel oxide powder , including low-pressure spray pyrolysis, surfactant mediated method, simple liquid phase process and other techniques. Mostly nickel oxide nano particles are prepared by the thermal decomposition of freshly prepared nickel hydroxide by sol-gel route at 300˚C.

Due to their special structures and properties, nickel oxide nanoparticles have been widely used in various fields such as photoelectric, recording, materials, catalyst, sensors, ceramic materials, etc. It is used in potential gas sensor for H2, in nanowires, nanofibres & specific alloys and catalyst application. Nickel oxide nanomaterials can be used in dye sensitized photocathode. These nanoparticles exihibit anodic electrochromism, excellent durability ,electrochemical stability, large spin optical density and various manufacturing possibilities. Also for low material cost as an ion storage material, NiO nanoparticle semiconductors became a motivating topic in the new area of research. Because of the volume effect, the surface effect and the macroscopic quantum tunnel effect, nanocrystalline NiO nanoparticles is expected to possess many improved properties than those of micrometer sized NiO particles. The nickel oxide nanoparticles are mostly used in batteries like lithium-ion batteries(LIB), nickel-iron battery, nickel-zinc battery, nickel cadmium battery etc. LIB has emerged as the primary source of power for variety of portable electronic devices. Here the anode material should possess low reduction potential and high specific capacity. Recently interest has been directed toward conversion reaction where nanostructured metal oxide are incorporated with a carbon-based support matrix and employed as LIB anode. Like many other nanostructured metal oxides, NiO has gained significant interest as LIB anode material because of its low cost, ease of synthesis, and environment friendly nature.

CHAPTER 2

SCOPE AND AIM OF PRESENT WORK

2. SCOPE AND AIM OF PRESENT WORK

The constant movement of the double bonds to stabilize the charge in the neighbor atoms causes, therefore, the movement of the charge, resulting in the conductivity. This movement of double bonds is called resonance and it describes the delocalized electrons within a molecule. A delocalized electron is an electron, presented in a π bond, which is shared by three or more atoms. Due to this process of the polaron formation, there is a change in the band structure of the conductive polymer. It creates the polaronic conduction bands, allowed bands in the bandgap, reducing the bandgap energy, making the polymer able to conduct,

1. Synthesis of PIN/NiO nanocomposites by a simple in-situ polymerization method
2. To study the interaction of polyindole/NiO nanocomposite by FTIR spectroscopy
3. To study the size and shape of the synthesized polymer nanocomposites using High-resolution transmission electron microscopy (HR-TEM)
4. To study the thermal stability of the prepared polymer nanocomposite by thermogravimetric analysis (TGA)

CHAPTER 3

EXPERIMENTAL PROCEDURE AND CHARACTERIZATION

3. EXPERIMENTAL TECHNIQUES

3.1. MATERIAL AND METHODS

Indole monomer (99%) was purchased from Fluka. Ferric chloride (FeCl3), chloroform ($CHCl_3$), and methanol were purchased from Merck India. Deionized water was used as a solvent for all the experiments. Chitosan nanoparticles with an average particle size of 70 nm were purchased from Sigma Aldrich.

3.2. SYNTHESIS OF POLYINDOLE

Polyindole (PIN) was synthesized by using the chemical oxidation method. The oxidant $FeCl_3$ (48 mmol) was dissolved in 30 mL of $CHCl_3$ and stirred well at room temperature. Similarly, an indole monomer (16 mmol) was dissolved in 40 mL of $CHCl_3$. The oxidizing agent ($FeCl_{3)}$ was added in a dropwise fashion into the indole solution. To obtain a total volume of 100 mL solution, an additional 30 mL of $CHCl_3$ was added into the indole/ $FeCl_3$ solution and the reaction mixture was stirred for 8 h under stirring at room temperature. At the end of the polymerization, the precipitate obtained in brown color was first filtered, washed with methanol, 100 mL of chloroform, and 100 mL of deionized water, respectively. Finally, powdered form PIN samples were dried for 24 h at 60°C in a vacuum oven.

3.3. SYNTHESIS OF POLYINDOLE/NICKEL OXIDE NANOCOMPOSITES

Chemically polymerized polyindole with different contents of nickel oxide nanocomposites were synthesized by in situ technique using FeCl3 as an oxidant in an aqueous medium. Firstly, different contents of NiO particles (3, 5, 7 and 10 wt. %) were dissolved in chloroform and it was then added to the indole monomer (16 mmol) dissolved in chloroform and ultrasonicated it for 30 min. 1 M of FeCl3 was dissolved in chloroform and was added to the above solution under vigorous stirring. This homogeneous solution was turned into a black colour indicating the polymerization reaction. The polymerization was carried out at room temperature for 8 h under stirring at room temperature. The precipitated PIN/NiO nanocomposite was filtered and rinsed with methanol, chloroform, and water. The prepared powder was vacuum dried for 24h at 60°C in a vacuum oven.

3.4 CHARECTERIZATION

3.4.1 FT-IR SPECTROSCOPY

Figure 1. FT-IR spectrometer

Fourier Transform Infrared (FT-IR) spectra of the sample were recorded by using a JASCO (model 4100) Fourier Transform Infrared Spectrometer in the region of 4000-400 cm−1. The new Jasco FT/IR-4100 is designed to provide operational features and sensitivity levels found only in more expensive instruments. The innovative technology incorporated in these instruments results in exceptionally high signal-to-noise ratio specifications. The model offers exceptional flexibility and can be easily upgraded to meet new requirements. Optional expandability includes microanalysis with an IR microscope, IR imaging with a multichannel microscope, and rapid scan option. The Jasco Quick Start System enables users of all experience levels to measure samples and perform data processing functions quickly and easily with a simple push of a button. Absorption bands in the spectrum result from energy change arising as a consequence of molecular vibrations of the bond stretching and bending type. The IR region covers 4000 to 400 cm−1. IR spectrum gave information about the structure of the compound. Since all the polymers prepared in the present investigation were solid, the samples were examined as KBr pellets.

3.4.2. High-Resolution transmission electron microscopy (HR-TEM)

High-resolution transmission electron microscopy (HRTEM) allows the direct imaging of certain composites. HRTEM, widely used in materials science, provides direct information on the local structural variability at the atomic level. However, a direct and phenomenological interpretation of the HRTEM micrographs is mostly not possible so that image processing and image simulations using theoretical structure models are inevitable. In HRTEM the structure of the specimen must be periodic in the direction of the transmitted electron beam. Therefore, only tilt boundaries can be studied where the tilt axis is parallel to the beam direction. Since the strong periodicity is disturbed in the core region of the boundaries, the point-to-point resolution of the instrument must be good enough so that information on the relaxation of atoms is transferred through the objective lenses despite the still rather high spherical aberration of the best lenses available to date. A high-resolution transmission electron microscope was carried out (JEOL; JEM–2100 HR, Japan) to study the size, shape, and dispersion of nickel oxide nanoparticles inside conducting polymer (PIN) matrix.

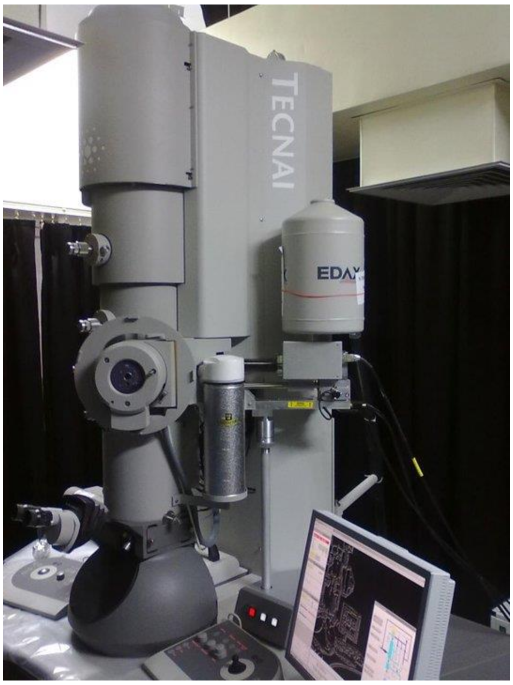


Figure 2. High Resolution transmission electron microscopy (HR-TEM) instrument.

3.4.3. THERMOGRAVIMETRIC ANALYSIS

Figure 3. Thermogravimetric analyser.

Thermal analysis of the material was studied by Hitachi STA7200 thermogravimetric analyser (TGA) was used for the studies. It is a computer-controlled instrument that permits the measurements of weight changes in the sample as a function of temperature or time. It is programmed in the required temperature range to measure the weight change resulting from the chemical reaction, decomposition, solvent and water evolution, Curie point transitions, and oxidation of the sample materials, etc. The temperature is scanned at a linear rate. The instrument supplied by Perkin Elmer had two components, an ultra-sensitive microbalance, and a furnace element. The balance is sensitive to 0.1 micrograms and the furnace could be heated from room temperature to 600℃ at a rate of 10℃ per minute. For purging tile sample holders, gases commonly used are oxygen, air (a mixture of 80% nitrogen and 20% oxygen), or nitrogen to study the oxidation, burning, and thermal stability of the materials. The purge gas flows directly over the sample. The recommended flow rate of the sample purge was kept less than the flow rate of the balance purge at all times. The thermal degradation behavior of the blend nanocomposites was determined by a thermogravimetric analyzer (TGA) between 30 and 750 ^{o} C with a 10 ^{o} C/min heating rate under a nitrogen atmosphere.

CHAPTER 4

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

4.1. FT-IR spectrum of PIN/NiO nanocomposites

The possible strong interactions or chemical reactions occurring between the nanoparticles and the macromolecular chain polymer nanocomposite can be illustrated with the help of Infrared spectra of the samples. Figure 4.1 shows the FTIR spectrum in the spectral range 4000-500 cm^{-1} of polyindole and NiO nanoparticles embedded PIN.

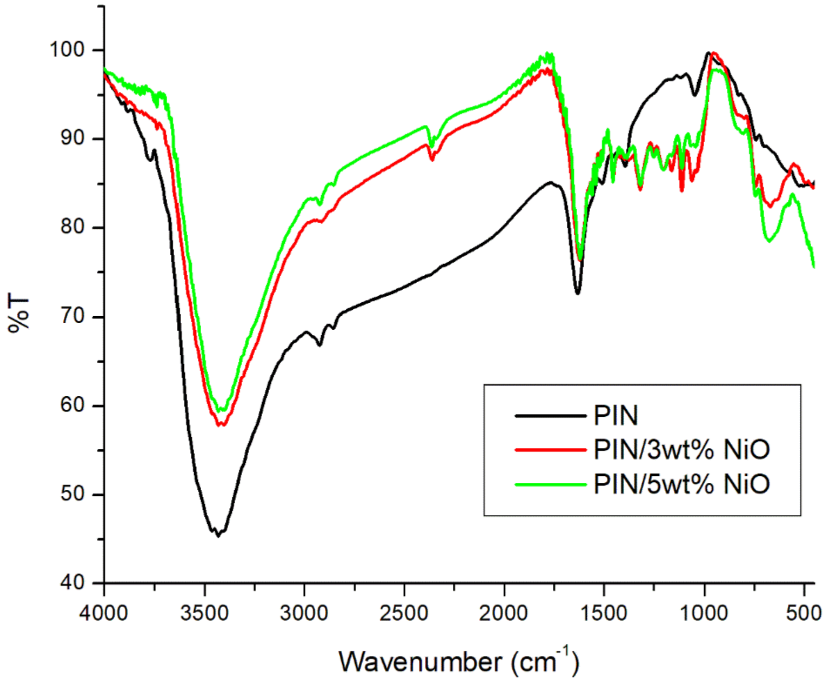


Figure 4.1. FTIR spectra of polyindole with different contents of NiO

The FTIR absorption signals of pure PIN are appeared at 3419, 1625, 1456, 1382 and 1118, 752 cm^{-1} which is in accordance with our previous research . The major peak at 3419 cm^{-1} is ascribed to the characteristic N-H stretching vibration of PIN. The peak at 1456 and 1382 cm^{-1} indicates C-N and C=N stretching of indole respectively. The bands at 1625 and 752 cm^{-1} are the characteristic stretching mode of benzene ring in PIN. So, it is evident that nitrogen atom of indole is not involved in the polymerization process. From the IR spectrum of composite, it can be seen that the characteristic peak of NiO is found to be located at 670 cm^{-1} confirms the presence of metal-oxygen bond in the PIN matrix. Furthermore, the band at 1625 found to be shifted to a lower wavenumber to 1605 cm^{-1} indicating the interaction of nanoparticles with the indole segments.

4.2. High Resolution Transmission Electron microscopy (HR-TEM)

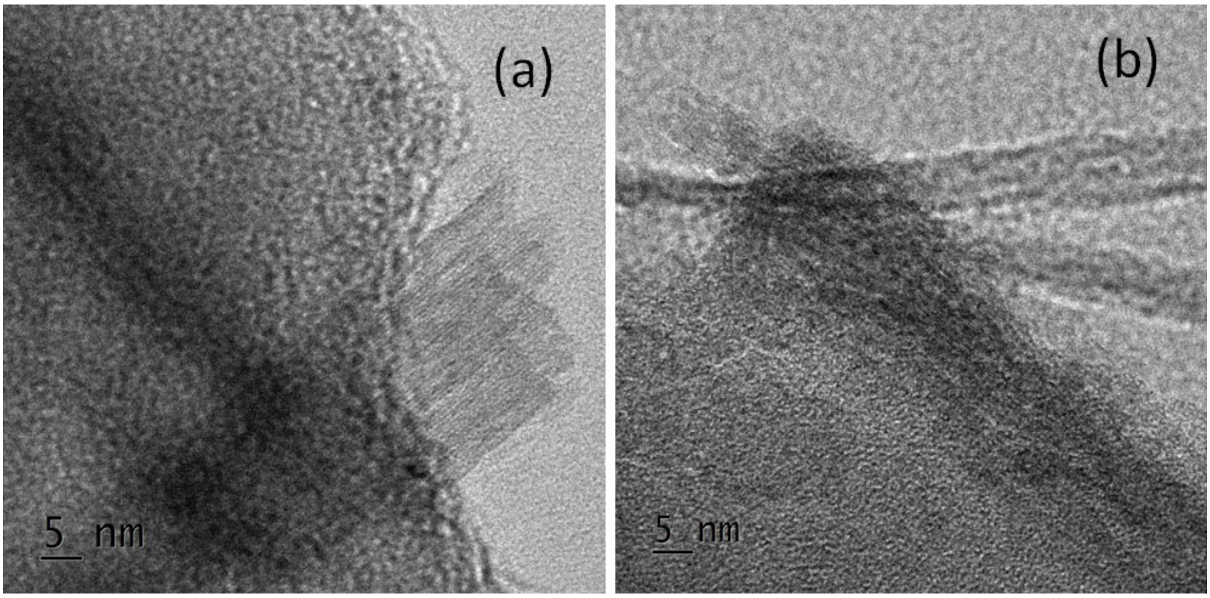


Figure 4.2. HR-TEM images of (a) PIN/5 wt. % NiO and (b) PIN/10 wt. % NiO

The transmission electron microscopic images of 5 and 15 wt% NiO nanoparticles incorporated PIN is given in Figure 4.2. The introduction of NiO nanoparticles in PIN is clearly visible in the TEM images of hybrid. It is found that the composite with 5 wt.% nanoparticles show a uniform arrangement of particles in polymer matrix. However, the TEM photograph of

PIN/NiO composite (10 wt.%) shows an irregular structure with respect to that of 5 wt. % of composites. At higher loading, the nanoparticles are randomly distributed within the polymer with few agglomerations of nanoparticles. With increasing loading of NiO nanoparticles there is not enough polymer chains to effectively utilise the surface of nanoparticles. At higher loading of fillers, the particle-to-particle distance is too short and which leads to the self-assembly of nanoparticles during the in-situ polymerization process.

4.3. Thermogravimetric analysis (TGA)

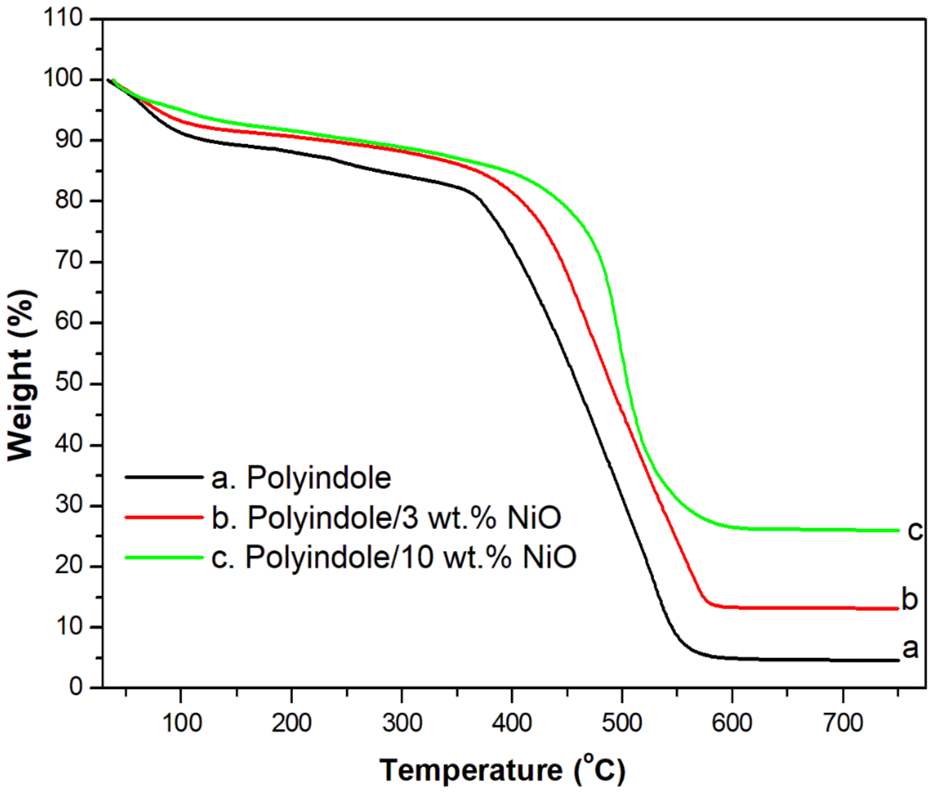


Figure 4.3. TGA curves of polyindole with different contents of NiO

The thermal stability of the polymer and its nanocomposites up to 800 ^{0}C has been assessed with the TGA. The TGA thermograms of PIN and PIN/NiO nanocomposites at different loadings are shown in Figure 4.3. All the samples showed two stages of weight loss. The initial weight (>127 ^{0}C) loss of PIN can be attributed to the loss of water molecules trapped on the surface, dimer, or unreacted monomer in the polymer. The second weight loss between 350 ^{0}C and 600 ^{0}C indicates the decomposition of organic components. In the case of PIN/ NiO nanocomposites, the thermal stability of all the samples is higher than the pure PIN. Furthermore, thermal stability increases with increase in contents of nanoparticles. For example, the major decomposition of PIN is occurring at 363 °C while the PIN with 3 and 10 wt. % NiO composites decomposes at higher temperature at 390 and 413 °C respectively. The final char residue obtained at 800 °C for pure PIN is only 6 % whereas the composite with 3 and 10 wt.% NiO incorporated samples are the final mass around 13and 24 % respectively at 800^{0}C. The higher thermal stability by incorporating inorganic phase into the polymer matrix is attributed to the strong interfacial interactions between the macromolecular chain of PIN and inorganic nanofillers.

CHAPTER 5

CONCLUSION

5. CONCLUSION

NiO nanoparticles embedded PIN with different filler ratios 0, 3, 5, 7 and 10. wt% was prepared by in-situ polymerization of indole. The formation of nanocomposites was studied by FT-IR spectroscopy. The morphology was studied using HR-TEM. The thermal stability of the synthesized composites was studied using thermogravimetric analysis (TGA). The shift in bands in IR spectra confirmed the interaction of nanofillers with PIN. TEM images indicated the lodging of nanofillers over PIN matrix and uniform dispersion of nanoparticles was obtained for the composite with 5 wt. % loading of fillers. The thermal stability and flame retardant properties of nanocomposites was higher than PIN and the thermal stability increases with increase in loading of fillers.

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