SYNTHESIS & CHARACTERISATION OF PANI/NiCo COMPOSITE

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This is hereby certify that the thesis entitled **"SYNTHESIS AND CHARACTERISATION OF POLYANILINE- NiCo COMPOSITE"** submitted by **Ms. Nidhi Rana**, THAPAR UNIVERSITY PATIALA(PUNJAB) is a record of research work carried out by her for the degree of **Master of Technology** under my guidance. This thesis is an original work of the candidate and to the best of my knowledge had not been submitted, in part or full, for any other degree or diploma in this or any other University. No portion of this thesis is a reproduction from any other source, published or unpublished, without acknowledgment.

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Nidhi Rana

[NIDHI RANA]

DEDICATED TO MY FAMILY

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CP	conducting polymers
PANI	polyaniline
PPy	polypyrrole
NiCo	nickel- cobalt alloy
APS	ammonium per sulphate
PVP	poly vinyl pyrolidone
CV	cyclic voltametery
ITO	indium tin oxide
XRD	X-ray diffraction
FTIR	fourier transform infrared spectroscopy
TEM	transmission electron microscope
TGA	thermogravimetric analysis
DSC	differential scanning calorimeter
rpm	rotation per minute
PANI/NiCo	composite of polyaniline and NiCo nano particles

LIST OF SYMBOLS

nm	nanometrer
μm	micrometer
mm	milimeter
A^0	angstronm
d	interplaner distance
K	Kelvin
Ω	ohm
R	resistance
ρ	resistivity
S/cm	siemen per centimeter
σ	conductivity
mg/mL	milligram per milliliter
T_g	glass transition temperature
t	time
^0C	degree celcius
eV	electron volt
kV	kilo volt
λ	wavelength

ABSTRACT

Films of polyaniline (PANI) and PANI/NiCo composites have been synthesized by spin coating technique. The NiCo powder of particle size 10-12nm was synthesized by chloride salts of nickel and cobalt and hydrazine hydrate as reducing agent. The polyaniline was synthesized by chemical oxidative polymerization of aniline. The composite films were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier transform infra red (FTIR) and the results were compared with polyaniline films. The thermal behavior was also observed which shows the greater stability of PANI/NiCo composite as compared to PANI. The conductivities of thin films were also calculated. The composite shows the greater value of the conductivity. The XRD pattern of the composite possesses a peak corresponding to the plane (531), which was not present in the NiCo powders. This may be attributed to the attachment of the polymer chains along this plane. The characteristic FTIR peaks of PANI were found to shift to higher wave number in PANI/NiCo composite. These observed effects have been attributed to interaction of NiCo particles with PANI molecular chains.

CHAPTER1

INTRODUCTION

This chapter includes the basic idea of conducting polymers, their conduction mechanism, synthesis techniques and application. The important type electro active polymer polyaniline is described in this chapter along with its composite.

CHAPTER1
INTRODUCTION TO CONDUCTING POLYMERS

1.1 INTRODUCTION

This chapter deals with the basic introduction to conducting polymers, their historical development, conduction mechanism, synthesis methods and applications. In this chapter there is also a discussion about an important conducting polymer that is polyaniline (PANI). The synthesis, structure and applications of this polymer are also discussed. In last the composites which are derived from polyaniline are also described. The composites of PANI with various types of nanoparticles are also referred in this chapter.

1.2 INTRODUCTION TO CONDUCTING POLYMERS

Conducting polymers exhibit semiconductor or metal-like electrical and optical properties while at the same time they are lightweight, flexible, inexpensive, and easy to synthesize [1]. Polymers are being discarded for their traditional roles as electric insulators to literally take charge as conductors with a range of novel applications. Scientists from many disciplines are now combining expertise to study organic solids that exhibit remarkable conducting properties. A large number of organic compounds, which effectively transport charge, are roughly divided into three groups i.e. charge transfer complexes/ion radical salts, organometallic species and conjugated organic polymers. A new class of polymers known as intrinsically conducting polymers or electroactive conjugated polymers has recently emerged. Such materials exhibit interesting electrical and optical properties previously found only in inorganic systems [2]. Organic conjugated polymer (conducting polymers) is mainly organic compounds that have an extended π-orbital system, through which electrons can move from one end of the polymer to the other. The conducting polymers are known to have considerable flexibility in chemical structures that can be modified. By chemical modeling and synthesis, it is possible to modulate the required electronic and mechanical properties of conducting polymers. Common classes of organic conductive polymer include poly (acetylene)s, poly (pyrrole)s, poly (thiophene)s, poly (terthiophene)s, poly (aniline)s, poly

(fluorine)s, poly (3alkylthiophene)s, polytetrathiafulvalenes polynapthalenes, poly (p-phenylene sulfide), poly (para-phenylene vinylene)s etc [3].An interesting property of conductive polymers is the change of their conductivity by many orders of magnitude upon oxidation or reduction. In electrochemical systems the switching between the conductive and the insulating states can be controlled by the electrode potential, which makes this class of polymers suitable for various sensor and electronic applications [4].

Table 1 *Conductivity of various metals, conducting polymers, semiconductors and insulators.*

MATERIAL	CONDUCTIVITY (S/Cm)
Gold, Silver, Copper	10^{6}
Doped trans- polyacetylene	10^{5}
Doped polyaniline	10^{1}
Germanium	10^{-2}
Silicon	10^{-6}
Undoped trans- polyacetylene	10^{-6}
Undoped polyaniline	10^{-10}
Glass	10^{-10}
Quartz	10^{-12}

1.3. HISTORICAL BACKGROUND OF CONDUCTING POLYMERS

The Nobel Prize in Chemistry, 2000, was awarded to Heeger, MacDiarmid and Shirakawa "for the discovery and development of electrically conductive polymers." However, there were several forerunners to these distinguished chemists. The most important representatives of the family of electrically conductive polymers, polyaniline and polypyrrole, were already being prepared by chemical or electrochemical oxidation in the nineteenth century. In fact, the discovery of polyacetylene in the 1970s—which had no practical importance but helped to arouse the interest of researchers and the public alike—was another episode in the history of conducting polymers [5].

Traditionally organic compounds were considered to be uniformly insulating [6]. In the 1950's, it was discovered that polycyclic aromatic compounds formed semi-conducting charge-transfer salts with halogens. This finding indicated that organic compounds could carry current. Organic conductors had been intermittently discussed and the area was energized by the prediction of superconductivity, following the discovery of BCS theory [7].The significance lies in the rediscovery of PA in 1977 by MacDiarmid and Heeger, University of Pennsylvania. They were able to enhance the electrical conductivity of PA (10^{-9} S/cm) by several orders i.e. 10^{-5} S/cm by simple doping with oxidizing agents e.g. AsF_5, $NOPF_6$ (p-doping) or reducing agents (n-doping) e.g. sodium napthalide. This has generated renewed interest of the scientific community towards the study and discovery of new conducting polymeric systems. After this a great increase in the conductivity of the poly-paraphenylene was noted. It forms highly conducting charge transfer complexes with both n and p type dopants. Doping with AsF_5 increases its conductivity to its values from 10^{-5} to 500 S/cm.

Beginning in 1963, Bolto and co-workers reported highly-conductivity in iodine-doped Polypyrrole [8, 9]. They achieved a conductivity of 1S/cm. These papers also describe the effects of iodine doping on conductivity, the conductivity type (n or p), and electron spin resonance studies on polypyrrole.

In 1974, McGinness and coworkers described an "active" organic-polymer electronic device, a voltage-controlled bistable switch. This device used DOPA melanin, a mixed copolymer of polyacetylene, polypyrrole and polyaniline, as the active element. The "ON" state of this

device exhibited almost metallic conductivity. Their material also exhibited classic negative differential resistance [10].

Three years after their report, Shirakawa et al. [5] described the conductive properties of iodine-doped, oxidized acetylene blacks. Based upon this (re)discovery, they received the 2000 Nobel Prize in Chemistry "For the discovery and development of conductive organic polymers".

1.4. CONDUCTION MECHANISM

The conduction mechanism in such polymers is very complex since such a material exhibits conductivity across a range of about fifteen orders of magnitude and many involve different mechanisms within different regimes. Conducting polymers show enhanced electrical conductivity by several orders of magnitude after doping. The concept of solitons, polarons and bipolarons has been used to explain the electronic phenomena in these systems. Conductivity in conducting polymers is influenced by a variety of factors including polaron length, the conjugation length, the overall chain length and by the charge transfer to adjacent molecules. These phenomenons can be explained by large number of models based on intersoliton hopping, hopping between localized states assisted by lattice vibrations, intra-chain hopping of bipolarons, variable range hopping in 3-dimensions and tunneling between conducting domains [2].

Although conducting polymers possess a relatively large number of delocalized pi electrons, a fairly large energy gap exists between the valence band and the conducting band (greater than 1 eV), thus these polymers are considered to be semi-conducting. These polymers must be doped (usually meaning altering the number of pi electrons) in order to render the polymers truly conducting. In conjugated polymers the electronic configuration is fundamentally different, where; the chemical bonding leads to one unpaired electron (the electron) per carbon atom. Moreover, bonding, in which the orbitals of successive carbon atoms along the backbone overlap, leads to electron delocalization along the backbone of the polymer.

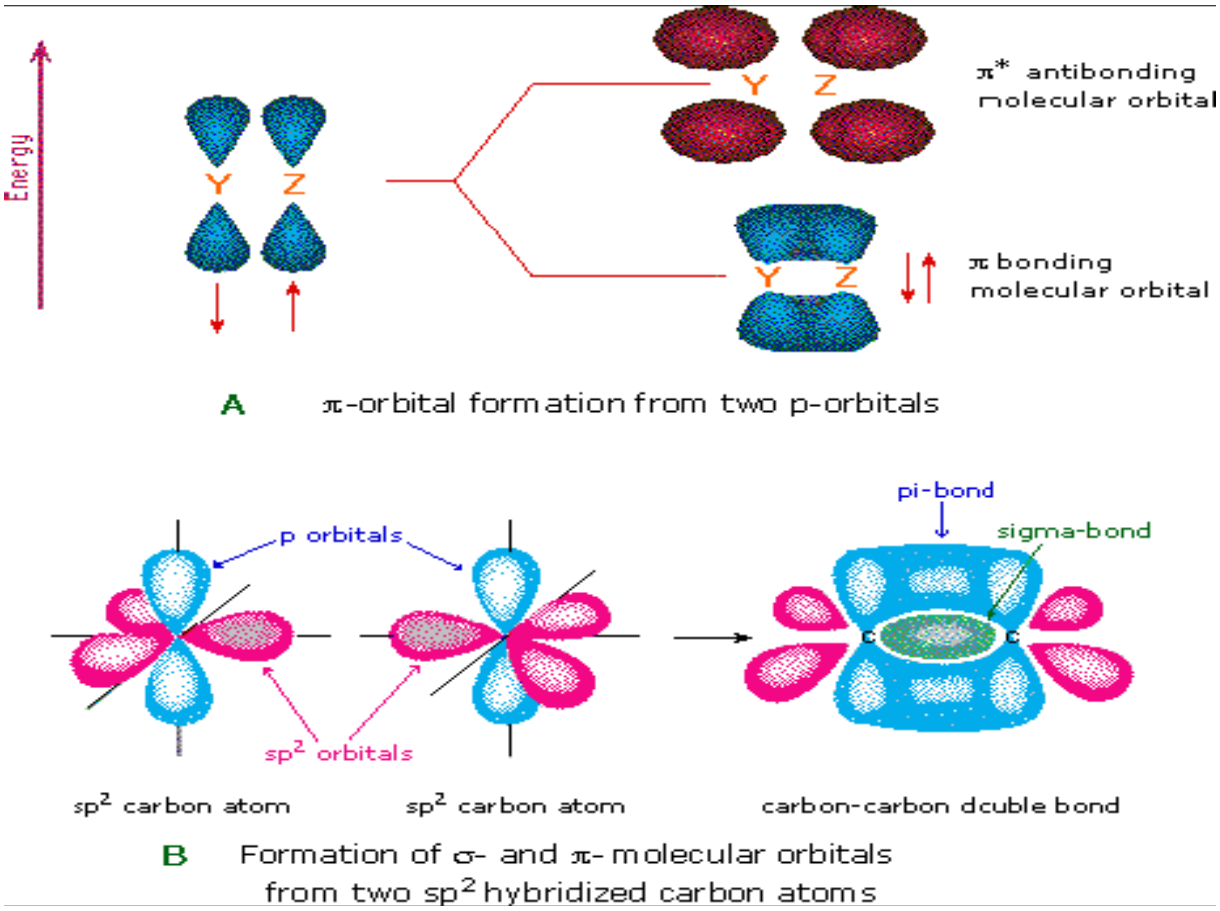


Fig.1.1 *Formation of molecular orbital*

One early explanation of conducting polymers is based on the band theory as a method of conduction. According to the band theory, a half filled valence band would be formed from a continuous delocalized π-system. This would be an ideal condition for conduction of electricity. However, it turns out that the polymer can more efficiently lower its energy by bond alteration (alternating short and long bonds), which, introduces a band width of 1.5 eV making it a high energy gap semiconductor. The polymer is transformed into a conductor by doping it with either an electron donator or an electron acceptor.

The bipolaron charge carrier exihibits relatively high energy, and thus is short- lived. Redistribution of charge and spin yields a polaron as the more stable charge carrier.A radical, cation, or anion defect on a polyacetylene backbone divides the polymer into sections which are mirror image to each other. The defect can move in either direction without affecting the

energy of the backbone. The movement of the defect can be describes as a solitary wave or solitons. The radical defect is referred to as solitons, the anion and cation defects are charged solitons. The neutral solitons have spin whereas the anion and cation defects are spineless. It has been shown that in strongly disordered CP, electron transport is dominated by hopping between conducting grains separated by insulating barriers. Although the nature of the metal-insulator transition is still a controversial topic in weakly disordered CP, several results indicate that heterogeneities play an important role. Thus, heterogeneous disorder seems to control the conductivity of a large majority of CP [11].

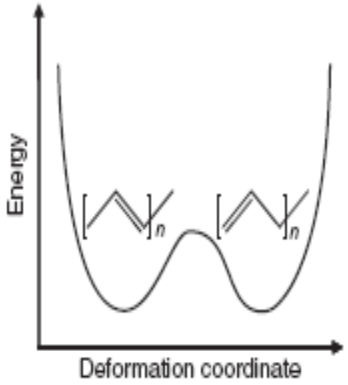


Fig.1.2 Energetically *equivalent forms of degenerate polyacetylene.*

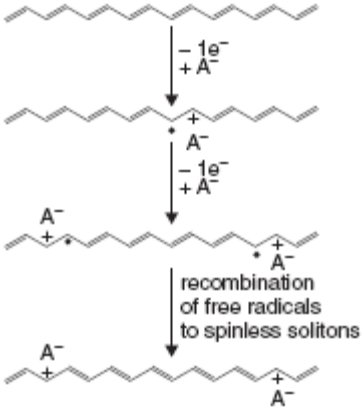


Fig1.3. *p-Type doping in polyacetylene*

The π-conjugated systems based on aromatic rings, such as polythiophene, polypyrrole, polyaniline, polyparaphenylene and their derivatives have nondegenerate ground states. In these polymers, the ground-state degeneracy is weakly lifted so that polarons and bipolarons (confined solitons pairs) are the important and dominant charge storage configurations In solid-state physics, a radical cation that is partially delocalized over a segment of the polymer is called a polaron. It is stabilized through the polarization of the surrounding medium, hence the name. Since it is really a radical cation, a polaron has spin 1/2. The radical and cation are coupled to each other via local resonance of the charge and the radical [13].

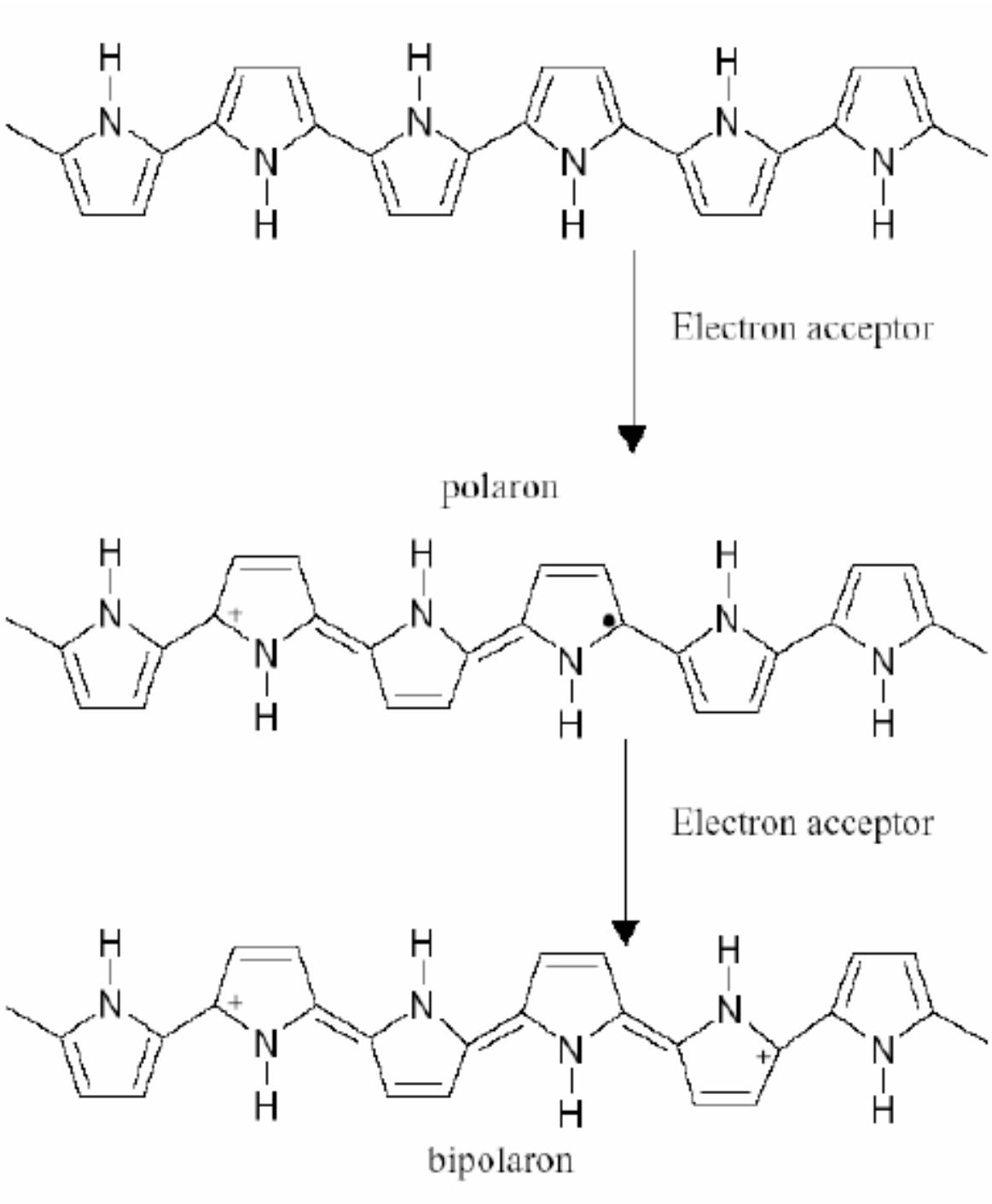
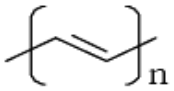
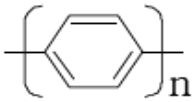
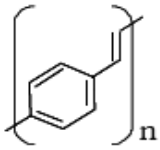
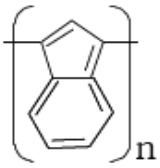
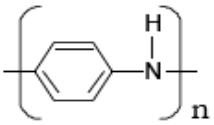
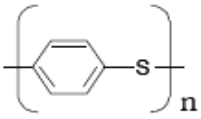
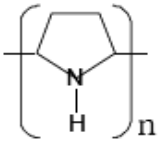
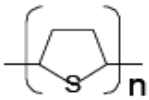
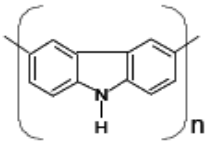
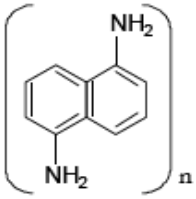


Fig.1.4 *Formation of polaron- bipolaron in a PPy chain*

The polymer may store charge in two ways. In an oxidation process it could either lose an electron from one of the bands or it could localize the charge over a small section of the chain. Localizing the charge causes a local distortion due a change in geometry, which costs the polymer some energy. However, the generation of this local geometry decreases the ionization energy of the polymer chain and increases its electron affinity making it more able to accommodate the newly formed charges. This method increases the energy of the polymer less than it would if the charge was delocalized and, hence, takes place in preference of charge delocalization. This is consistent with an increase in disorder detected after doping by Raman spectroscopy. A similar scenario occurs for a reductive process [12]. Although solitons and bipolarons are known to be the main source of charge carriers, the precise mechanism is not yet fully understood. The problem lies in attempting to trace the path of the charge carriers through the polymer.

All of these polymers are highly disordered, containing a mixture of crystalline and amorphous regions. It is necessary to consider the transport along and between the polymer chains and also the complex boundaries established by the multiple numbers of phases. This has been studied by examining the effect of doping, of temperature, of magnetism and the frequency of the current used. These test show that a variety of conduction mechanisms are used. The main mechanism used is by movement of charge carriers between localized sites or between solitons, polaron or bipolaron states. Alternatively, where inhomogeneous doping produces metallic islands dispersed in an insulating matrix, conduction is by movement of charge carriers between highly conducting domains. Charge transfer between these conducting domains also occurs by thermally activated hopping or tunneling. This is consistent with conductivity being proportional to temperature [13].

Table 2 *Conductivity of some common conducting polymers.*

Conducting Polymer	Structure	Conductivity (S/cm)
Polyacetylene		~ 1000
Polyparaphenylene		100 ~ 500
Polyparaphenylene vinylene		~ 3
Polyazulene		~ 0.1
Polyaniline		1 ~ 100
Polyparaphenylene sulfide		1 ~ 100
Polypyrrole		40 ~ 100
Polythiophene		10 ~ 100
Polycarbazole		10 ~ 100
Polydiaminonaphthalene		10^{-3}

1.5 SYNTHESIS OF CONDUCTING POLYMERS

Various methods are available for the synthesis of conducting polymers. However, the most widely used technique is the oxidative coupling involving the oxidation of monomers to form a cation radical followed by coupling to form di-cations and the repetition leads to the polymer. Electrochemical synthesis is rapidly becoming the preferred general method for preparing electrically conducting polymers because of its simplicity and reproducibility. The advantage of electrochemical polymerization is that the reactions can be carried out at room temperature. By varying either the potential or current with time the thickness of the film can be controlled. Electrochemical polymerization of conducting polymers is generally employed by: (1) constant current or galvanostatic; (2) constant potential or potentiostatic; (3) potential scanning/cycling or sweeping methods. Standard electrochemical technique which employs a divided cell containing a working electrode, a counter electrode and a reference electrode generally produces the best films. The commonly used anodes are chromium, gold, nickel, palladium, titanium, platinum and indium-tin oxide coated glass plates.

1.6. APPLICATIONS OF CONDUCTING POLYMERS

The extended π-systems of conjugated polymer are highly susceptible to chemical or electrochemical oxidation or reduction. These alter the electrical and optical properties of the polymer, and by controlling this oxidation and reduction, it is possible to precisely control these properties. Since these reactions are often reversible, it is possible to systematically control the electrical and optical properties with a great deal of precision. It is even possible to switch from a conducting state to an insulating state. In electronics the main advantage of the use of polymers is the ease at which they can be processed into required shapes. The resulting circuits are lightweight and flexible, but not yet as fast as silicon components. There are so many applications of the conducting polymers. We can divide these applications in two broad categories. They are given in table 3.

TABLE 3. *Different applications of the CP*

Group 1	Group 2
Electrostatic materials	Molecular electronics
Conducting adhesives	Electrical displays
Electromagnetic shielding	Chemical biochemical and thermal sensors
Printed circuit boards	Rechargeable batteries and solid electrolytes
Artificial nerves	Drug release systems
Antistatic clothing	Optical computers
Piezoceramics	Ion exchange membranes
Active electronics (diodes transistors)	Electromechanical actuators
Aircraft structures	'Smart' structures
	Switches

Conducting polymers are now widely used in the design of electrochemical biosensors. Conductive polymers improve the sensitivity and selectivity of electrochemical sensors and biosensors due to their electrical conductivity or charge transport properties [3]. Recently, conducting polymers have attracted much interest in the development of biosensors. The electrically conducting polymers are known to possess numerous features, which allow them to act as excellent materials for immobilization of bio molecules and rapid electron transfer for the fabrication of efficient biosensors. Many papers have been reviewed the salient features of conducting polymers and their wide applications in health care, food industries, environmental monitoring etc [2].

The volume change induced by the oxidation–reduction of inherently conducting polymers (ICPs) has led to their use in so-called artificial muscles. A solution-processable polythiophene demonstrated large electrochemically induced strain up to 11.5%. The largest strain □11.5% was obtained in an electrolyte solution consisting of 0.1M Li.TFSI (lithium triflouromethanesulfonimide) in acetonitrile. The maximum strain attainable increased with an increase in the anodic potential applied and decreased with an increase in stimulation frequency or increasing mechanical load. Such functionalized polythiophene material has the combined advantage of solution processability and the ability to produce large strain [14].

Low-Voltage Polymer Field-Effect Transistors Gated via a Proton Conductor [15]. Polymeric Elements for Adaptive Network [16], Polymer Electrolyte-Gated Organic Field-Effect Transistor [17] has been fabricated using conducting polymers.

Another application of the conducting polymer is the corrosion protection. The synthesis of polythiophene and polypyrrole top coatings was successfully achieved on graphite modified polymer coatings. The coated systems were shown to decrease the corrosion of stainless steel (SS), by acting as physical barrier on the surface and exhibiting anodic protective behavior on SS. The intercalation of graphite layer has improved the protection efficiency of polymer films, lowering the water mobility and permeability against corrosive environment. Especially the polypyrrole coating system was shown to exhibit almost a perfect coating behavior, for considerably long immersion period [18].

1.7 POLYANILINE (PANI)

1.7.1 Introduction

Polyaniline is unique among conducting polymers in its wide range of electrical, electrochemical and optical properties as well as good stability. Polyaniline can be doped to highly conducted state by protonic acids or by electrochemical methods and show moderate conductivity upon doping. The electrical and sensing properties of the polyaniline may be increased by formation of composites with various types of particles. It is one of the so-called doped polymers, in which conductivity results from a process of partial oxidation or reduction. Polyaniline compounds can be designed to achieve the required conductivity for a given application. The resultant blends can be as conductive as silicon and germanium or as insulating as glass. Another advantage is that it is both melt and solution processable. This means that the compound can be easily mixed with conventional polymers and that it is easy to fabricate polyaniline products into required shapes.

1.7.2 Structure of PANI

Polyaniline is a typical phenylene based polymer having a chemically flexible –NH group in a polymer chain flanked either side by a phenylene ring. It can also be defined as the simple

1, 4- coupling product of monomeric aniline molecule. The protonation and deprotonation and various other physio-chemical properties of polyaniline is due to the presence of the NH- group. One of the most known and detailed investigated conducting polymer is polyaniline (PANI), a compound existing in many different oxidation states which conductivity strongly depends on protonation with organic or inorganic acids. The most common green protonated emeraldine has conductivity on a semiconductor level of the order of 100 S cm–1, many orders of magnitude higher than that of common polymers (<10^{-9} S/cm) but lower than that of typical metals (>104 S/cm). Protonated PANI, (e.g., PANI hydrochloride) converts to a non-conducting blue emeraldine base when treated with ammonium hydroxide [19].

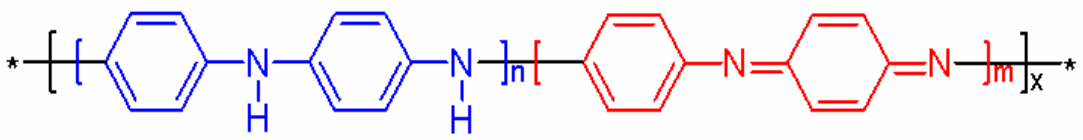


Fig.1.5 *Structure of polyaniline*

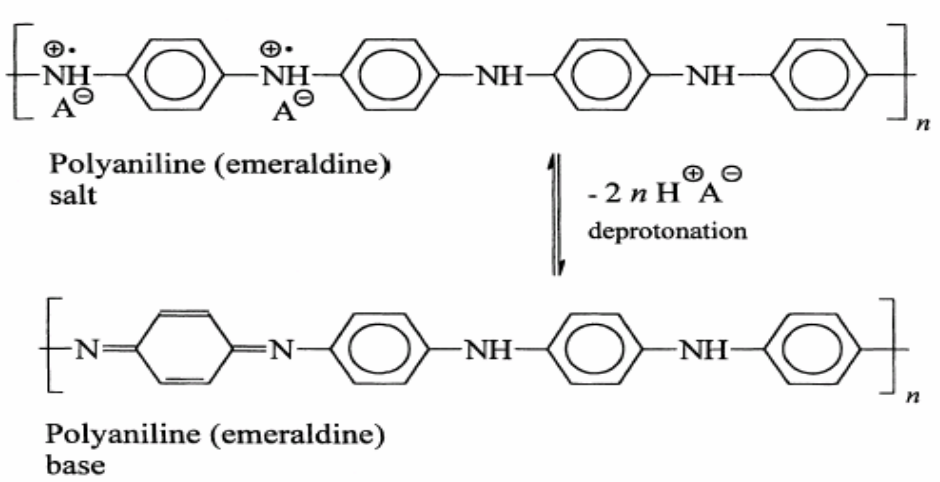


Fig1.6 *PANI (emeraldine) salt is deprotonated in the alkaline medium to PANI (emeraldine base. A is an arbitrary anion.*

Polyaniline exists in four main oxidation states viz.

1. Leucoemeraldine base,
2. Emeraldine base and
3. Emeraldine salt,
4. Pernigraniline.

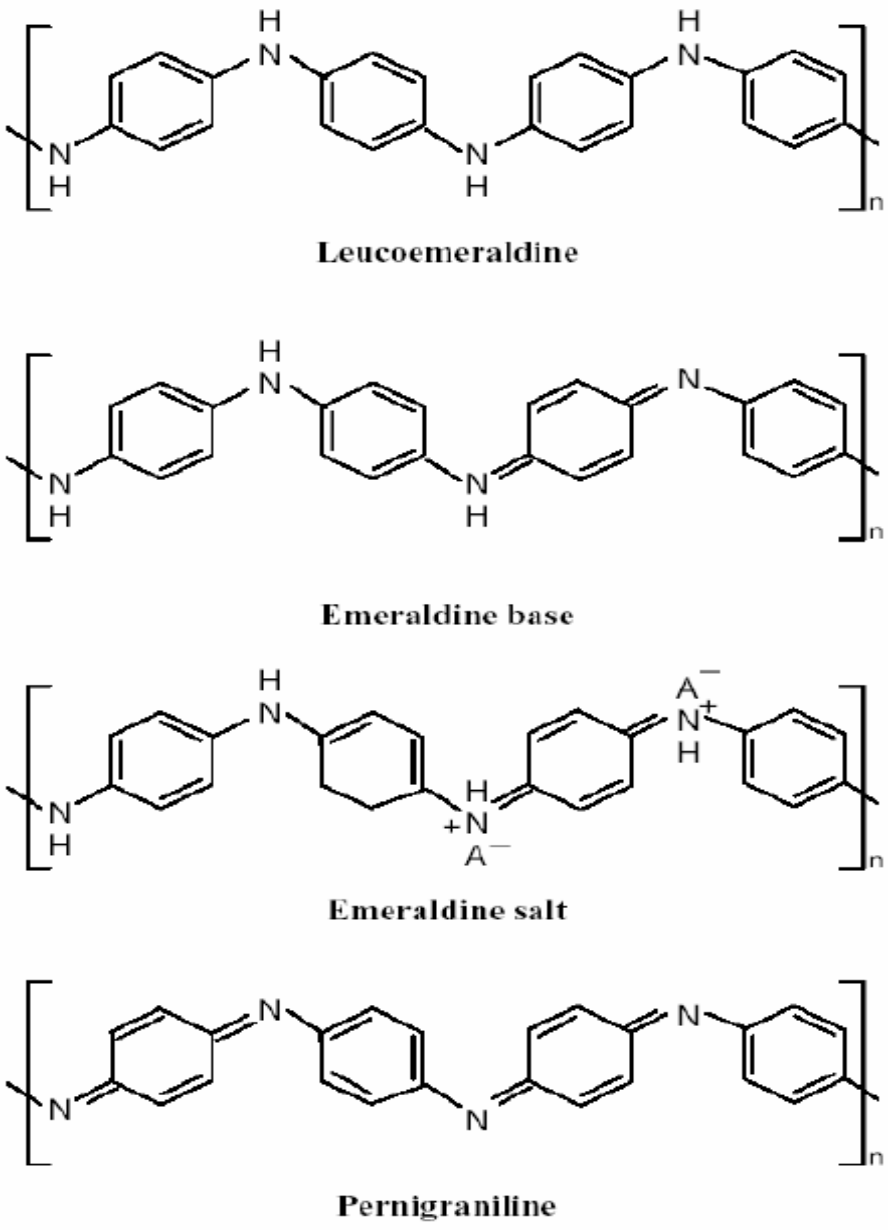


Fig.1.7 *Oxidation states of polyaniline*

A research paper shows that the polaron-lattice band structure fully accounts for the observed x-ray transitions. A finite spectral intensity of Kα is observed at the Fermi level for protonated polyemeraldine, supporting the applicability of the polaronic-metal model for highly conducting polymers [20].

1.7.3 Synthesis of PANI

Oxidation of aniline is the most employed synthetic route to polyaniline and can be performed either electrochemically or chemically. Reaction is usually carried out in acidic medium with a chemical oxidizing agent such as ammonium persulphate. Branching or even cross linking during polymerization occur through the formation of radicals at the 2 & 6 position. In the literature there are many methods for the polymerization of the aniline monomer. Some of these methods will be discussed in next chapter.

1.7.4 Composite of PANI

Composites of different compositions can be obtained using conducting polymer matrix. Polyaniline is widely used as the matrix for dispersing various types of filler materials (e.g. metal powder, flakes, carbon black). Conducting polymer PANI composites have various applications in electronic and electrical fields. PANI/inorganic nanostructures are important class among these composites.

They combine mechanical flexibility, optical and electrical properties of conducting polymers with the high electrical conductivity and magnetic properties of metal nanoparticles. Three main types of inorganic nonmaterials are used as inorganic fraction.

1. Metal oxide nanoparticles.
2. Metal nanoparticles.
3. Carbon nanotubes.

The first interesting type is metal oxide, which can improve the properties of PANI in the field of electricity, magnetism, etc. The second type is metal nanoparticles. Up to now, many PANI/metal composites such as PANI/Au, PANI/Ag and PANI/Ni nano composites have been prepared using chemical or electrochemical method. The third main type of inorganic nonmaterial is carbon nanotube, which could improve the conductivity of PANI.

The incorporation of metal nanoparticles into the conducting polymer offers enhanced performance for both the host and the guest [21]. They have diverse application potentials in electronics because incorporation of metal clusters is known to increase the conductivity of the polymer [22]. The polymer–metal nanocomposites are promising candidates based on the fact that the small sized particles enhance the properties while the polymer matrix offers flexible functionalities to control host–guest interaction to ensure the growth and distribution of metal nanoparticles.

1.7.5 Applications of PANI and its composites

The conductivity of polyaniline makes it an ideal shield against discharges of static electricity. That is why polyaniline based composites and compounds have been used in the packaging of electronics products. Polyaniline composites are being tested for use against electromagnetic radiation Manufacturers hope that one day printed circuit boards, electro chromic windows in houses and cars and conductive fabrics will contain polyaniline compounds.

Polyaniline shows reversible insulator-to-metal transitions and electrochromic behavior (yellow–green–blue–violet) depending on its oxidation state and pH. It has good stability in the presence of air and humidity. The combination of these characteristics makes polyaniline useful for various applications including rechargeable batteries, light emitting diodes, transistors molecular sensors, nonlinear optical devices, corrosion protection, electromagnetic interference shielding, and electro chromic displays. However, limitations such as poor solubility in common solvents and infusibility have been an impediment to its incorporation into industrial applications. Preparation of composites of conducting polymer (PANI) has been considered to provide a suitable solution to the processibility problem. These composites have the ability to enhance their material properties with desirable mechanical and physical characteristics [13, 23].

CHAPTER2

LITERATURE REVIEW

i

In this chapter there is review of the work of some researchers related to polyaniline and its composites. The methods of their synthesis and the applications are reviewed from the literature.

CHAPTER2
LITERATURE REVIEW

2.1 INTRODUCTION

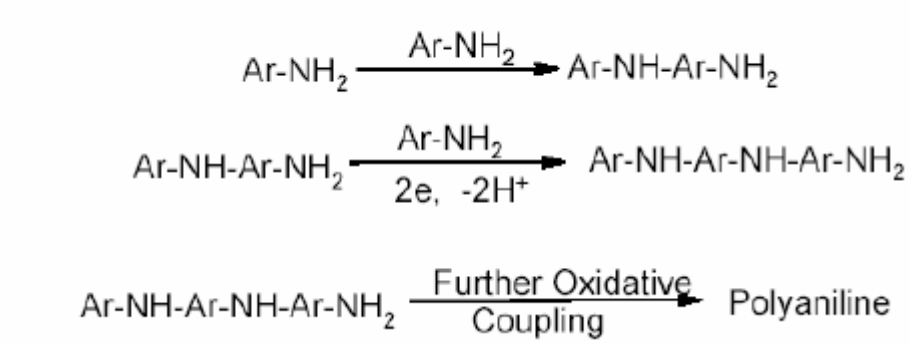
In this chapter work of some earlier researchers have been discussed briefly. Literature review is confined to polyaniline and its composites; thin film development and their applications in different fields.

2.2 PANI- DEVELOPMENT AND SYNTHESIS

Yuvraj Singh Negi et al. [24] have reviewed recent research work on polyaniline-type conducting polymers. Research and development work had been reviewed with special interest in chemical, electrochemical, doping processes, and polyaniline-based composite processes. Process development with high accuracy of product results had the direct relationship with structure and properties. According to them, polyaniline based on a variety of structures generated from molecular structural modification could give more interesting results for future applications.

2.2.1 Chemical synthesis

ROSA VERA A**.** et al. [25] carried polymerization of aniline. The synthesis was based on mixing aqueous solutions of aniline hydrochloride and ammonium peroxydisulfate at room temperature, followed by the separation of PANI hydrochloride precipitate by filtration and drying. The synthesis of the PANI can be described in following steps,



M. Sacak et al. [26] prepared two solutions, one with the oxidizing agent ammonium per sulfate ($(NH_4)_2$ (S_2O_8)) and the other the monomer: aniline ($C_6H_5NH_2$) or ortho-methoxyaniline (C_7H_9NO). Both precursors were dissolved in electrolytic media of: 1M CF_3COOH; 1M HCI - 1M NaCl; and 1M H_2SO_4 - 0.5 M Na_2SO_4. Table represents the different electrolytes used in the chemical synthesis carried out in this work.

Table 4 *Electrolytes used in the synthesis of polymers.*

POLYMER	ELECTROLYTE
P 1	PANI -1M CF_3COOH
P 2	POMA-1M CF_3COOH
P 3	PANI - 1M NaCl - HCI
P 4	POMA - 1M NaCl - HCI
P 5	PANI - 0.5 M Na_2SO_4 - 1M H_2SO_4
P 6	POMA - 0.5 M Na_2SO_4 - 1M H_2SO_4

Solutions were cooled at 0 ± 0.1 ^oC and stirred for 2 hours under nitrogen atmosphere. The precipitate formed (polymer) was filtered under vacuum and washed with acetone. Afterward, both PANI and POMA polymers were treated with ammonium hydroxide for de protonation and kept for 16 hours. After that these solutions were filtered and dried under vacuum. Conductive form of polyaniline was synthesized by the anodic and chemical oxidation of aniline in malonic acid medium. The conductivity of polyaniline doped with malonic acid changed from 1.62 x 10^{-6} to 2.5 x10^{-5} S/cm depending on the way it was synthesized. The polymer growth rate was observed to be very slow in malonic acid compared with H_2SO_4. Thermo gravimetric data revealed that the maximum thermal reaction rate of PANI doped with malonic acid was at 200^0C and 520^0C compared with 290^0C and 530^0C of the polymer doped with H_2SO_4. A conductive PANI can be synthesized in malonic acid solution using both chemical and electrochemical routes. The electrochemical polymer growth rate in malonic acid media was much slower than that observed in H_2SO_4.

2.2.3 Electrochemical synthesis

According to the study of Bekar Sari et al. [27] conductive homopolymers of o-chloroaniline, p- bromoaniline and N-methylaniline were synthesized electrochemically in perchloric acidic solution and their properties were analyzed. Initially, the maximum oxidation potential values of these monomer solutions were determined by Cyclic Voltammetry (CV). These conductive polymers were synthesized under a nitrogen atmosphere using a potentiostat.

Majjidi et al. [28] worked out that the synthesis of optically active polyaniline salt films has been achieved via the enantioselective electro polymerization of aniline on indium-tin-oxide (ITO)-coated glass electrodes in the presence of sulphonic acid. They found the similar results as were obtained under potentiostatic, galvanostatic and potentiodynamic conditions. Results suggest that chiral holes might be formed in the polymer matrix during both redox and chemical re-doping cycles of polyaniline salt films.

2.3 COMPOSITES OF POLYANILNE

Y.-N. Qi et al. [29] synthesized Polyaniline/Al_2O_3 (PANI/ Al_2O_3) composites by in-situ polymerization at the presence of HCl as dopant by adding Al_2O_3 nanoparticles into aniline solution. The composites were characterized by FTIR and XRD. The thermogravimetry (TG) and modulated differential scanning calorimetry (MDSC) were used to study the thermal stability and glass transition temperature (*T*g) of the composites, respectively. The results of FTIR showed that Al_2O_3 nanoparticles connected with the PANI chains and affected the absorption characteristics of the composite through the interaction between PANI and nano-sized Al_2O_3. The results of XRD indicated that the peaks intensity of the PANI/ Al_2O_3com posite were weaker than that of the pure PANI. From TG and derivative thermo gravimetry (DTG) curves, it was found that the pure PANI and the PANI/ Al_2O_3 composites were all one step degradation. Moreover the PANI/ Al_2O_3 composites were more thermal stable than the pure PANI. The MDSC curves showed that the nano-sized Al_2O_3 increased the glass transition temperature (*T*g) of PANI.

Pilli Satyananda Kishore et al. [30] used Phosphomolybdate has been employed simultaneously as the oxidizing agent for the monomer polymerization and the reduced polyoxometalate is used as reducing agent for the reduction of metal ions. The composites thus obtained have been characterized and may have many potential applications. Furthermore, the method can be extended to the synthesis of other conducting polymers and opens up a new route to prepare inorganic–organic nanocomposites with wide variation of properties. These composites may have applications in wide area like sensors and catalysis.

R. Del RIÂO et al. [31] synthesized a composite of polyaniline and carbon black by electrochemical method. The potential of a Pt electrode in a solution containing aniline and carbon black suspension is cycled to obtain desired composite. Carbon black and SDS (sodium dodecyl sulphate, which was used as additive) in the forming electrolyte have a pronounced effect on the kinetics of polymerization. It is possible to obtain rather porous films in much shorter time than that employed to obtain films of PANI without any additive or carbon black. The presence of carbon black particles embedded in the polymer film does not seem to modify the intrinsic electronic properties of the composite, though the substantial increase in the composite film capacity is probably due to its higher surface area.

Nirmalya Ballav at al. [32] synthesized composite of PANI with CoO by chemical route. They used ammonium vanadate/ H_2SO_4 system as oxidizing agent during polymerization. The aqueous solution of MoO_3 was used in the reaction mixture. The composite was characterized by FTIR, thermo gravimetric study and XRD.

2.4 THIN FILMS OF PANI AND PANI- COMPOSITES

Hu Yan et al. [33] prepared the film of polyaniline by solution casting. Polyaniline was chemically prepared using ammonium persulphate as oxidizing agent. Polyaniline films were prepared by casting an N-methyl-2-pyrrolidone (NMP) solution of an emeraldine base of polyaniline powders on glass substrates at 50^0C. The films were mechanically stretched by hand with a hand-made stretching machine at 100^0C. Finally, the films were doped in 1 M HCl aqueous solution. With doping the polyaniline, changes to conducting form. The films thus obtained have thickness of 20μm.

J. Jaczewska et al. [34] developed the polyaniline film using spin coating technique. The polymers were dissolved in analytical- grade common solvents (chloroform, THF, and cyclohexanone) to form solutions of pure polymers (with a concentration of 30 mg/mL) and symmetric (1:1 w/w) polymer blends (with a constant concentration of 20 mg/mL). The pure polyaniline films were prepared using the solution of PANI in solvent and spin coated onto Si/SiO_2 substrate at a speed of 3000 rpm.

X H Xia et al. [35] prepared a highly porous NiO/polyaniline (PANI) composite film on ITO glass by combining the chemical bath deposition and electro-polymerization methods, successively. The porous NiO film acts as a template for the preferential growth of PANI along NiO flakes, and the NiO/PANI composite film has an intercrossing net-like morphology. The electrochromic performance of the NiO/PANI composite film was investigated in 1 M $LiClO_4$+1 mM $HClO_4$/propylene carbonate (PC) by means of transmittance, cyclic voltammetry (CV) and chronoamperometry (CA) measurements. The NiO/PANI thin film exhibits a noticeable electrochromism with reversible color changes from transparent yellow to purple and presents quite good transmittance modulation with a variation of transmittance up to 56% at 550 nm. The porous NiO/polyaniline (PANI) composite film also shows good reaction kinetics with fast switching speed, and the response time for oxidation and reduction is 90 and 110 ms, respectively.

CHAPTER3

EXPERIMENTAL DETAILS

This chapter includes the detailed description of the procedure, chemicals and equipments used to synthesis the desired product.Various characterization techniques to characterize the materials are also discussed.

CHAPTER3
EXPRIMENTAL DETAILS

3.1 INTRODUCTION

This section of thesis deals with the details of the various experiments which have been carried out to synthesis the desired product. Various techniques used to characterize the material are also discussed. Chemicals and equipment which are used during experiments are also described in this chapter. The flow chart showing the systematic experimental work is as follow:

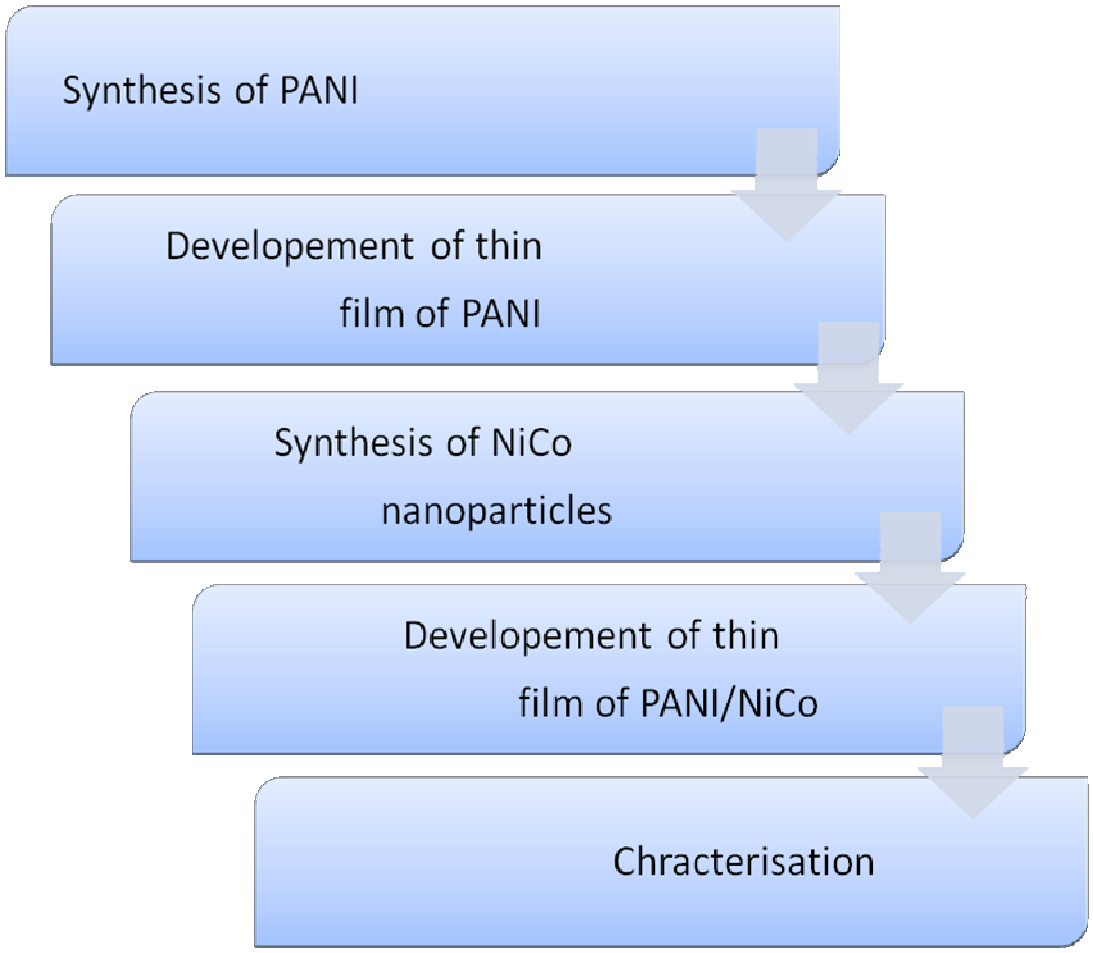


Fig.3.1 *Flow chart of the various steps of experimental work.*

3.2 CHEMICAL USED

A large number of chemicals were used to synthesis PANI, NiCo nanoparticles and their composite. The following table describes the name of chemical their common designation and source which supplied the chemical.

Table 5 List *of chemicals.*

S.NO.	NAME OF CHEMICAL	CHEMICAL FORMULA	SOURCE
1	ANILINE	$C_6H_5NH_2$	Spectrochem ltd. Mumbai
2	HYDROCHLORIC ACID	HCl	RFCL ltd. New Delhi
3	AMMONIUM PERSULPHATE	$(NH_4)_2(S_2O_8)$	Spectrochem ltd. Mumbai
4	CYCLOHEXANONE	$(CH_2)_5CO$	Spectrochem ltd. Mumbai
5	NIKEL CHLORIDE	$NiCl_2.6H_2O$	Spectrochem ltd. Mumbai
6	COBALT CHLORIDE	$CoCl_26H_2O$	Loba chemicals
7	POLYVINYL PYROLIDONE	$(C_6H_9NO)_n$	Spectrochem ltd. Mumbai
8	ETHYL ALCHOHOL	C_2H_5OH	Loba chemicals
9	SODIM HYDROXIDE	NaOH	S.D. fine chemical ltd.
10	HYDRAZINE HYDRATE	$N_2H_4.H_2O$	Loba chemicals
11	ACETONE	CH_3COCH_3	SDFCL Mumbai
12	DE IONIZED WATER	H_2O	Spectrochem ltd. Mumbai
13	CHLOROFORM	$CHCl_3$	Spectrochem ltd. Mumbai
14	METHANOL	CH_3OH	Spectrochem ltd. Mumbai

3.3 EQUIPEMENT AND THEIR DETAILS

Various equipments were used in the laboratory to synthesis PANI, nanoparticles and to develop the thin films. These equipments are discussed along with their uses are given in present investigation.

3.3.1 Electronic weighing machine

The desired quantities of the chemicals were measured using METTLER TOLEDO AX 205 Electronic weighing machine (Maximum: 205 gm; d = 0.01mg) during synthesis of PANI powder and NiCo nanoparticles.

3.3.2 Filter assembly

Filter assembly was used to separate the precipitate of the PANI powder from the solution. This assembly contains flask, buckle funnel, vacuum pump and filter paper.

3.3.3 Heating oven The precipitates were dried in a heating oven in which the temperature can rise to a maximum 300^0C.

3.3.4 Magnetic stir

Magnetic stir was used to mix the two solutions or to mix the powder in a solution. This equipment is based upon the theory magnetic force. A magnetic bead is put in the mixture of the compounds which has to be mix. Then magnetic field produced by the stirrer exerts force on the magnetic bead and it starts moving. A cycle of magnetic field rotates the bead and it mixes the two solutions. Speed of rotation may be varied in this equipment.

3.3.5 Centrifuge machine

The synthesized nanoparticles were separated out from the solution using centrifuge machine (SIGMA Laboratory Centrifuge 3K3O), shown in the photograph 1.

Centrifuge machine is based upon the principle of centrifugal force. When a particle moves in a circle outward force acts on it. The solution is placed in the centrifuge tubes and machine applies centrifugal force on the particles which are dispersed in the liquid. Due to this force the particles settled down and solution become clear.

PHOTOGRAPH 1 *Centrifuge equipment.*

3.3.6 Vacuum Rotavapor

The powder form of NiCo nano-particles was dried using BUCHI Rotavapor R-205, Vacuum controller V-800, BUCHI heating bath B-490. The equipment is shown in photograph 2. The temperature was kept 40^0C of heating bath. This equipment based on the principle that the evaporation occur at fast speed at low pressure at a given temperature. During drying process the pressure is kept at minimum value by varying it from the pressure panel. This leads to fast drying of the solution which contains nanoparticles.

PHOTOGRAPH 2 *Vacuum Rotavapor*.

3.3.7 Spin Coater

Model APEX SCU 2005 was used to develop the thin film of PANI and composite of PANI/ NiCo. The photograph of the instrument is shown below.

PHTOGRAPH 3 *Spin coater unit.*

Spin coating is the preferred method for application of thin, uniform films to flat substrates. This process is very simple, illustrated in Figure 3.1. An excess amount of polymer solution is placed on the substrate. The substrate is then rotated at high speed in order to spread the fluid by centrifugal force. Rotation is continued for some time, with fluid being spun off the edges of the substrate, until the desired film thickness is achieved. The solvent is usually volatile, providing for its simultaneous evaporation [36].

Spin Coating involves the acceleration of a liquid puddle on a rotating substrate. The coating material is deposited in the center of the substrate either manually or by a robotic arm. The physics behind spin coating involve a balance between centrifugal forces controlled by spin speed and viscous forces which are determined by solvent viscosity.

The spin coating technique consists of four basic stages:

1. The polymer is dispensed onto the wafer

2. The polymer is spread across the wafer (by spinning at approximately 500 rpm)
3. The wafer is then spun at a higher speed (2000-4000 rpm)
4. The "edge bead" is removed using a backside wash cycle which causes solvent to curl back over the lip of the wafer and wash off the "bead" that is created due to the surface tension at the edge of the wafer.

Some variable process parameters involved in spin coating are:

- Solution viscosity
- Solid content
- Angular speed
- Spin Time

The film-forming process is primarily driven by two independent parameters – viscosity and spin speed. The range of film thicknesses easily achieved by spin coating is 1-200µm. For thicker films, high material viscosity, low spin speed, and a short spin time are needed. However, these parameters can affect the uniformity of the coat. Multiple coatings are preferred for a film thickness greater than 15µm.

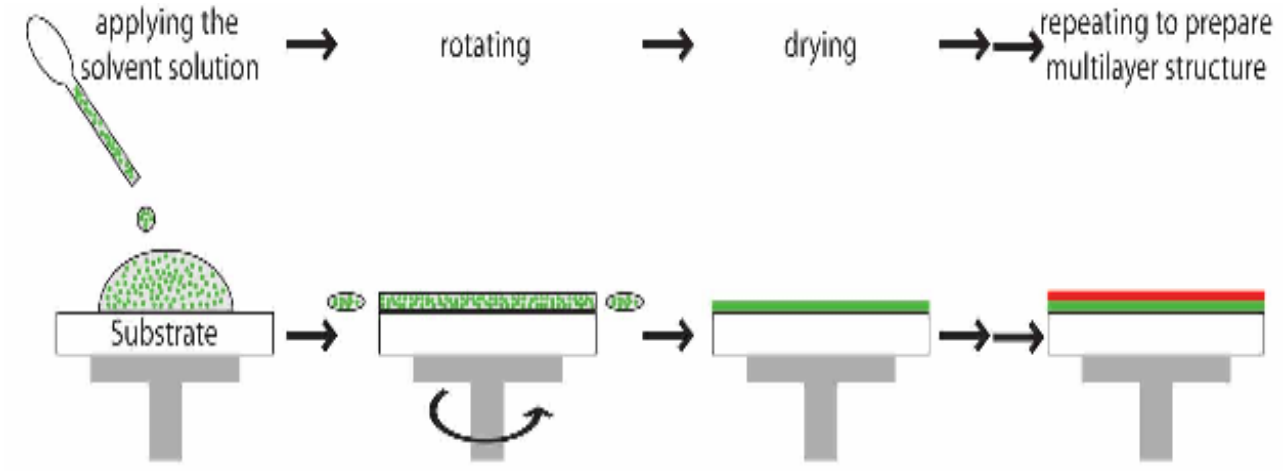


Fig3.2 *Various steps of spin coating.*

3.4 CHARACTERISATION TECHNIQUES

Various techniques are used to characterize the thin film of PANI, PANI/NiCo composites and nanoparticles. These techniques are discussed below:

3.4.1 X-ray diffraction

XRD pattern were recorded with a X'PERT PANALYTICAL diffractometer using Cu (Kα) radiation (λ= 1.5406 Å) at room temperature. This technique is based on the Braggs law of diffraction. The compact X-ray diffraction instrument is shown in photograph 4.

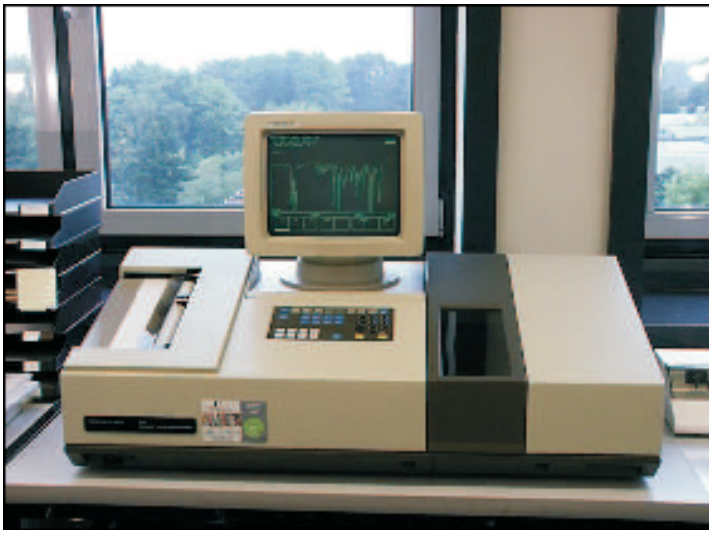
PHOTOGRAPH 4 *XRD analysis instrument.*

An X-ray tube generates X-rays by focusing an electron beam that has been accelerated across a high voltage field and bombards the stationary rotating solid target. As electrons collide with atoms in the target and slow down, a continuous spectrum of X-rays are emitted, which is termed as Bremsstrahlung radiation. The high energy electrons also eject inner shell electrons in atoms through the ionization process. When a free electron fills the shell, an X-

ray photon with energy characteristic to the target material is emitted. Common targets used in X-ray tubes include Cu and Mo, which emit 8 keV and 14 keV with corresponding wavelength of 1.54 A^0 and 0.8 A^0, respectively. X-rays primarily interact with electrons in atoms. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystal, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern there- fore allows us to deduce the distance between the crystal planes [38, 39].

3.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of the prepared samples were recorded in KBr powder using Perkin Elmer RX-1 FTIR spectrophotometer in the range 500 cm^{-1} to 3500 cm^{-1}. The instrument is shown below in photograph 5.



PHOTOGRAP 5 *FTIR spectrophotometer*

Infra-red spectroscopy is particularly applicable to the study of orientation in polymers. Infra-red absorbance is due to the interaction between the electric field vector and the molecule dipole transition moments due to molecular vibrations. The absorbance is at a maximum when the electric field vector and the transition moment are parallel to each other,

and zero when the orientation in perpendicular. The orientation of molecular components can be characterized by using the dichroic ratio which is defined as $A_{//}/A_{\perp}$ where $A_{//}$ is the absorbance parallel to the chain axis and $A_{\perp}$ is the perpendicular direction [40, 41].

Different alignment of the molecules results in changes in the intensity of a number of infra-red modes and therefore is an indicator of crystalline nature, because each interatomic bond may vibrate in several different modes (stretching or bending). Individual bond may absorb at more than one IR frequency. Stretching absorptions usually produce stronger peaks than bending, however the weaker bending absorptions can be useful in differentiating similar type of bonds (e.g. aromatic substitution). It is also important to note that symmetrical vibration do no cause absorption of IR radiation. In general, the most important factors determining where a chemical bond will absorb or not are the bond order and type of atoms joined by the bond. Conjugation and nearby atoms shift the frequency to a lesser degree. Therefore, the same or similar functional group in different molecules will typically absorb within the same and specific frequency range. Hooke's law states that the IR frequency at which a chemical bond absorbs is inversely proportional to the square root of the reduced mass of the bonded atoms.

3.4.3 Thermal Analysis instrument

TGA-DSC analysis was carried out using Water model SDT-Q-600MENT. The ramping rate was kept 5^0C/min in nitrogen flow in the temperature range of 30- 1000 ^{0}C. This instrument is shown in photograph 5.

This instrument provides simultaneous measurement of weight change (TGA) and differential heat flow (DSC) from ambient to 1500 °C. SDT technology features a dual beam thermo balance that compensates for beam growth and buoyancy contributions to baseline drift; thermocouples that provide differential temperature measurements (DTA) within the dual ceramic beams; and a purge gas system with digital mass flow control, gas switching capability and a separate gas inlet for the option to deliver reactive gas to the sample. For analyzing samples that tend to lose weight during heating, the new Q600 technology provides

improved DSC accuracy when the instantaneous weight, rather than the initial sample weight, is used in heat flow integration. The DSC signal is also useful in providing higher temperature solid state phase and melting transitions where no weight loss occurs.

Photograph 6 *TGA-DSC Instrument*

Differential Scanning Calorimet Thermogravimetry analysis (TGA) is a technique by which the mass of a material is measured as a function of temperature while the material is subjected to a controlled temperature program. On the TGA curves the mass is normally plotted on the Y-axis and temperature is on X-axis increasing from left to right. (DSC) is a technique to measure the heat flow through the sample as the sample is heated at a controlled heating rate. Heat flow is dependent on sample morphology. If the material is amorphous, a shift in the base line will be observed when the amorphous chains are given enough thermal energy to facilitate movement of chains. Thus, the material changes from rigid glassy state to rubbery state as the chains become more flexible and a change in heat capacity occurs. The temperature at which this change in material properties occurs is referred to as the glass transition temperature (Tg). If the material is crystalline, a peak in the heat flow occurs as the crystals melt or crystallize [42].

3.4.4 Transmission Electron Microscope (TEM)

TEM measurements were performed on a JEOL-1200EX TEM instrument operated at 120 kV. This instrument was used to see the smaller features of the composite material and the nanoparticles. The TEM micrographs were taken for the composite PANI/NiCo and NiCo composite.

For preparation of samples for TEM analysis, a portion of composite film was scratched and was dispersed in an ethanol solution and deposited on carbon-coated Cu-TEM grids. The film on the TEM grid was allowed to stand for some time to allow the liquid to evaporate. After drying, the specimen is transferred in the microscope column for imaging at different magnification and the electron diffraction patterns were recorded [43].

TEM images are formed using transmitted electrons (instead of the visible light) which can produce magnification details up to 1,000,00X with resolution better than $10A^0$. The images can be resolved over a fluorescent screen or a photographic film. Furthermore the analysis of the X-ray produced by the interaction between the accelerated electrons with the sample allows determining the elemental composition of the sample with high spatial resolution. At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging [37].

3.4.5 Mechanical profiler

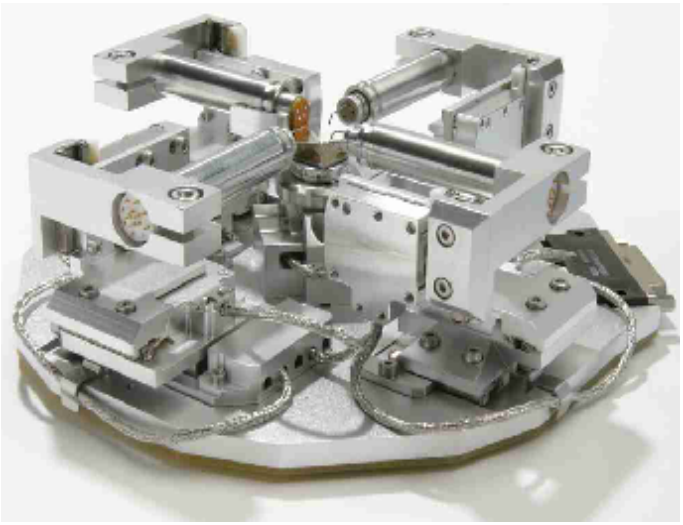
The thickness of the thin film was measured using TALYSURF SERIES 2 INSTRUMENT. There are many different optical (classical interferometry, holographic interferometry, moiré methods, speckle techniques and white light interferometry) and mechanical techniques used to measure surface shape and roughness. The Form Talysurf series 2 instrument is a mechanical profilometer, it means, that mechanical transducer, called a stylus, is dragged across a surface and its movement in the vertical direction is recorded to obtain a surface profile.

PHOTOGRAPH 7 *Mechanical profiler.*

Stylus (90° conical diamond stylus with the spherical tip of 2 mm radius) is carried at one end of a beam pivoted at the fulcrum on knife edges. The remote end carries an armature which moves between two coils, changing their relative inductance. The signal is amplified by special gauges are also used in the newer types of measuring instruments, where the range to resolution ratio has increased from approx 1000:1 to better than 64 000:1. Raw profile was measured across cooper film boundary on glass base. Using reference point is possible to specify value of film thickness [44].

3.4.6. Semiconductor characterization

I-V characteristics of thin films of PANI and PANI/NiCo composite measured using KEITHLEY 4200 SEMICONDUCTOR CHRACTERISATION UNIT. The photograph of the instrument is given below. The thin film of PANI and composite was placed on the probe table. The silver paste was applied at the two ends of the film. The tungsten probe made to touch these contacts, and the current through the film was measured at different voltages. This measurement was used to calculate the resistivity and hence the conductivities of the thin films.



PHOTOGRAH 8 *Probe station used to probing the sample.*

3.5 PROCEDURE FOR SYNTHESIS OF POLYANILINE

The detailed procedure for the synthesis of polyaniline is given below.

5cc of aniline monomer was taken in a beaker and ice cooled by putting in it a refrigerator. After it 100 ml solution of 2M HCl was prepared. Then ice- cooled aniline monomer was added in the 100 ml HCl, by continues shaking. This mixture of solution was put in the refrigerator at zero degree.

In a separate beaker 8-10 gm of ammonium persulphate (APS) was added in min water (about 30-50 ml). This is called APS solution and it oxidizes the monomer of aniline. The mixture of monomer and HCl was put in ice cubes so that the temperature would maintained at zero degree. After that APS solution was added dropwise to the monomer mixture by constant stirring (monomer mixture was put on the magnetic stir). Green precipitate started to appear which indicated the polymerization of the monomer unit. After mixing solution was kept overnight, so that the polymerization may completed.

Next day the solution was filtered and washed with distilled water. As prepared powder was dried at 55 ^{0}C. The green powder was the conducting polymer powder and called as emeridine salt. To convert this salt to emeridine base form 50 ml ammonia solution was added to conducting powder. The solution was stirred overnight. And again the solution was filtered and dried at 55^{0}C.

3.6 THIN FILM DEVELOPMENT OF POLYANILINE

Thin films of PANI have been developed by spin coating method. The procedure for spin coating of PANI is discussed here. First of all a suitable solvent was chosen to dissolve aniline. Various solvents have been tried to synthesize the thin film of polyaniline. However cyclohexanone was found suitable for the purpose of spin coating. Its viscosity and drying factors were optimum. The aniline was dissolved in cyclohexanone with a concentration of 30mg/ ml. the solution was stirred for 5-6 hours. After stirring, the solution was centrifuged at a speed of 3000 rpm, to settle the undissolved polyaniline. The clear solution of PANI in cyclohexanone was obtained. This solution was used to grow the thin film of polyaniline.

The glass substrate (at which the thin film is to be grown) was put on the stage of the spin coater. The vacuum pump was then turned on. This vacuum sticks the glass substrate to the rotating stage firmly. The speed of the motor was set to 600 r.p.m. and time was set to 15 sec. After it a drop of the PANI solution is put in the center of the glass substrate with the help of dropper. After it the spin coater started at the speed 600 r.p.m. During rotation the speed was again set to 1200 rpm.for next 30 sec. and again the coater was set to rotate at 1200 r.p.m. for 30 sec. After the rotation has stopped, the vacuum pump was turned off and the glass substrate was taken out. A blue colored film was obtained. The as prepared film is thin film of non-conducting PANI. this film was made conducting after doping 2M HCl. The film was dipped in the HCl for 2-3 seconds. The color of the film changed to green which indicated that it had become conducting a shown in the photograph 9.

PHOTOGRAPH 9 *Thin film of PANI on glass substrate.*

3.7 PROCEDURE FOR THE SYNTHESIS OF NICO ALLOY NANOPARTICLES

The procedure for the synthesis of NiCo alloy nano-particles were same as given by in the reference [45]. The nickel-cobalt alloy nanoparticles were synthesized using chloride salts of nickel and cobalt. Ethyl alcohol was used as solvent. PVP was used as surfactant and capping agent. It prevents the agglomeration of the nanoparticles. Hydrazine hydrate+ sodium hydroxide was used as reducing agent. It reduces the metal salt into the metal particles. Acetone was used as dispersing agent to disperse the nanoparticles in the solution so that they may not be settled down. The nanoparticles are collected from the solution form by means of centrifuge machine. After it particles were washed with a mixture of methanol and Chloroform (1:1 ratio). As such prepared powder was dried to get the nanoparticles.

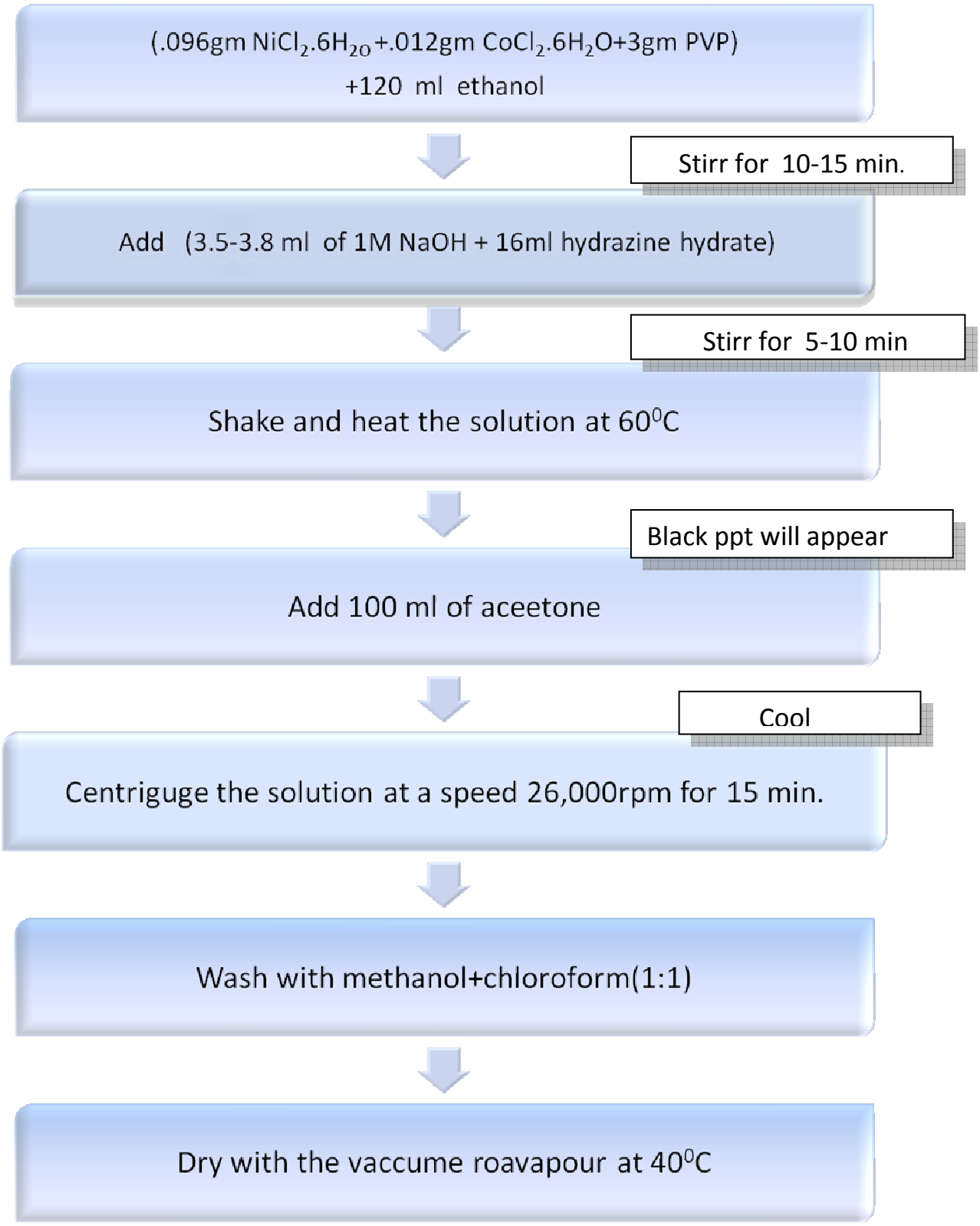


Fig. 3.3 Synthesis *procedure for NiCo nanoparticles.*

3.8 THIN FILM DEVELOPMENT OF PANI/NiCo COMPOSITES

The undoped form of PANI was dissolved in cyclohexanone and a clear solution was obtained as described in the section 3.7. As prepared 2ml solution was taken. The NiCo composite with undoped PANI was prepared by adding 20% NiCo nanoparticles (0.04 gm in 2ml) in the clear solution of undoped PANI in cyclohexanone. The solution was then kept on stir for 6-7 hours.

The thin film of the PANI/NiCo composites were developed using spin coating technique. The similar process was employed as described in the case of polyaniline. The rotation speed of the machine was set 600 rpm for 30 second and after it at 1000 rpm for 20 seconds. The thin films of these composite materials are shown in photograph 10.

PHOTOGRAH 10 *Thin film of PANI/NiCo composite.*

CHAPTER4

RESULT AND DISCUSSION

This chapter includes the different results which obtained by various characterization techniques and the various results are discussed to reach a conclusion.

CHAPTER4

RESULT AND DISCUSSION

4.1 NTRODUCTION

This chapter carries the detail discussion of the results which are obtained by various characterization techniques. The different results of the composite material are compared with matrix material and particulate materials.

4.2 THICKENESS MEASURMENT

The thickness of the composite material deposited over a glass slide was measured using mechanical profilometer. The films were developed in such a way that the half portion of the glass substrate was coated and other half was uncoated. A mechanical transducer dragged over the covered and uncovered surface and hence there is a step while going from left to right. Hence the thickness can be easily calculated by subtracting the vertical position of the transducer (when it was dragged over the uncoated surface) from its position when it was dragged over the coated surface. Hence there was a step at origin. The graph which is showing the thickness of the thin film is given at next page fog.4.1. From the graph it is clear that,

Thickeness of the film (t) = 258.9449µm – 257.8379µm

‘t’= 1.107µm

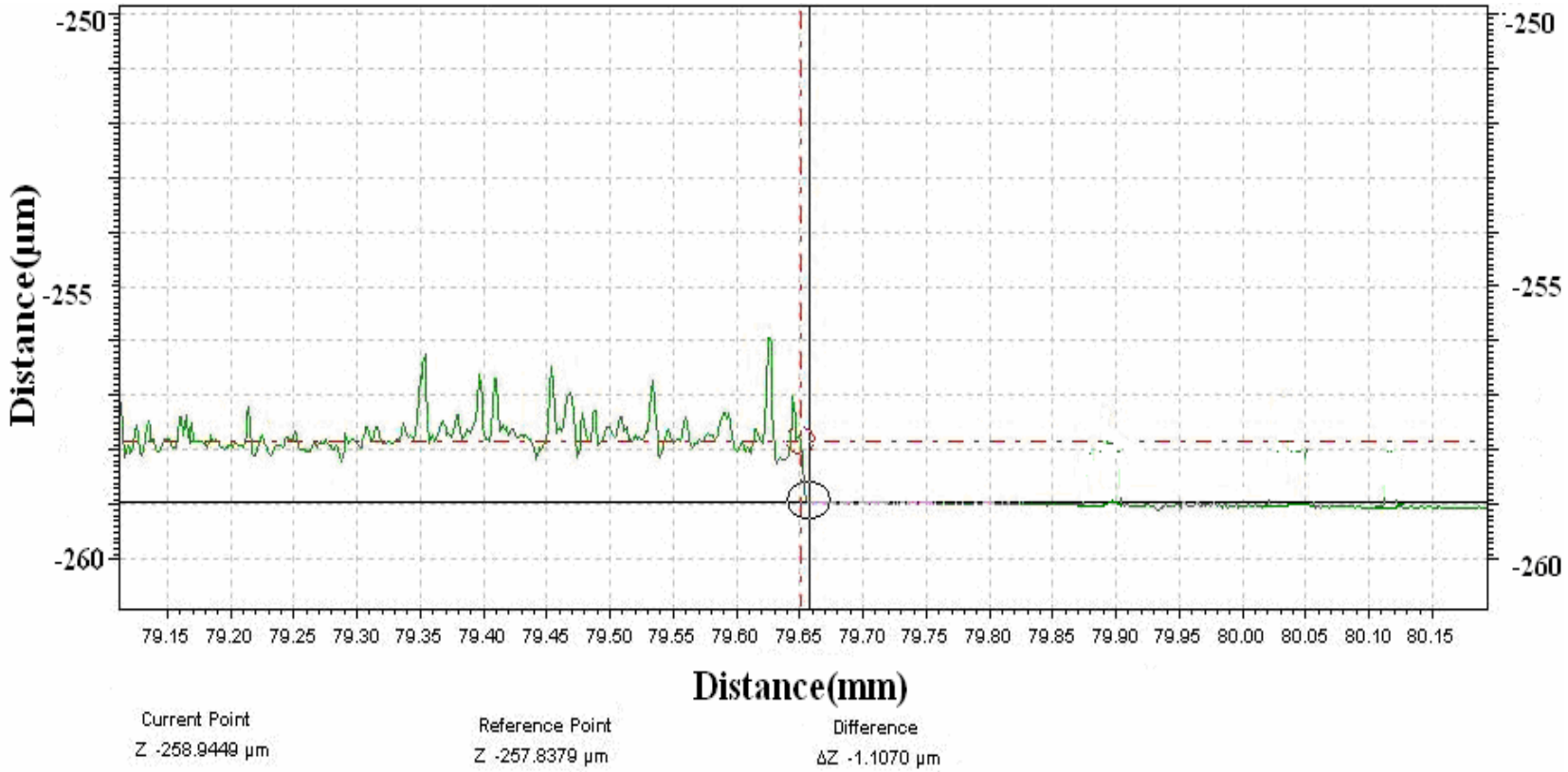


Fig. 4.1 *Thickeness mesurement graph of thin film*

4.3 X-RAY DIFFRACTION

The results of x-ray diffraction are shown in following figures (4.1 - 4.3). It is clear from the pattern that there is no sharp peak in the XRD pattern. There is a broad hump at position $2\theta = 22^0$ as shown in fig.4.1. It shows that the PANI is amorphous in nature. This result is in agreement which has been reported in literature [46].

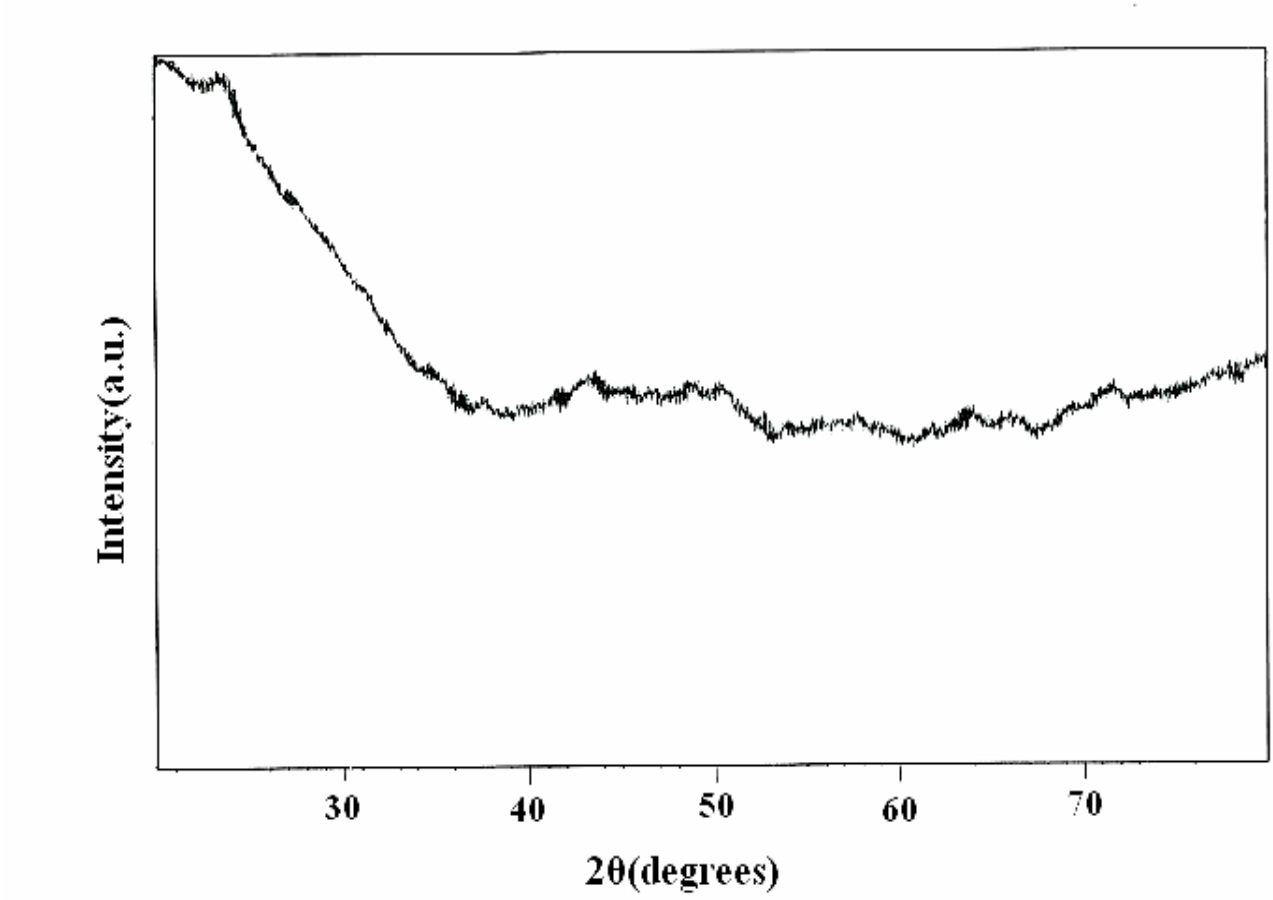


Fig. 4.2 *XRD pattern of PANI.*

The characteristic peaks at 44.50°, 51.80° and 76.40° (Fig. 4.2) correspond to Miller indices (100), (200) and (220), indicating the formation of nickel/cobalt alloy particles with face-centered-cubic (fcc) structure[47]. From the XRD pattern the size of the particle is calculated using Scherer formula.

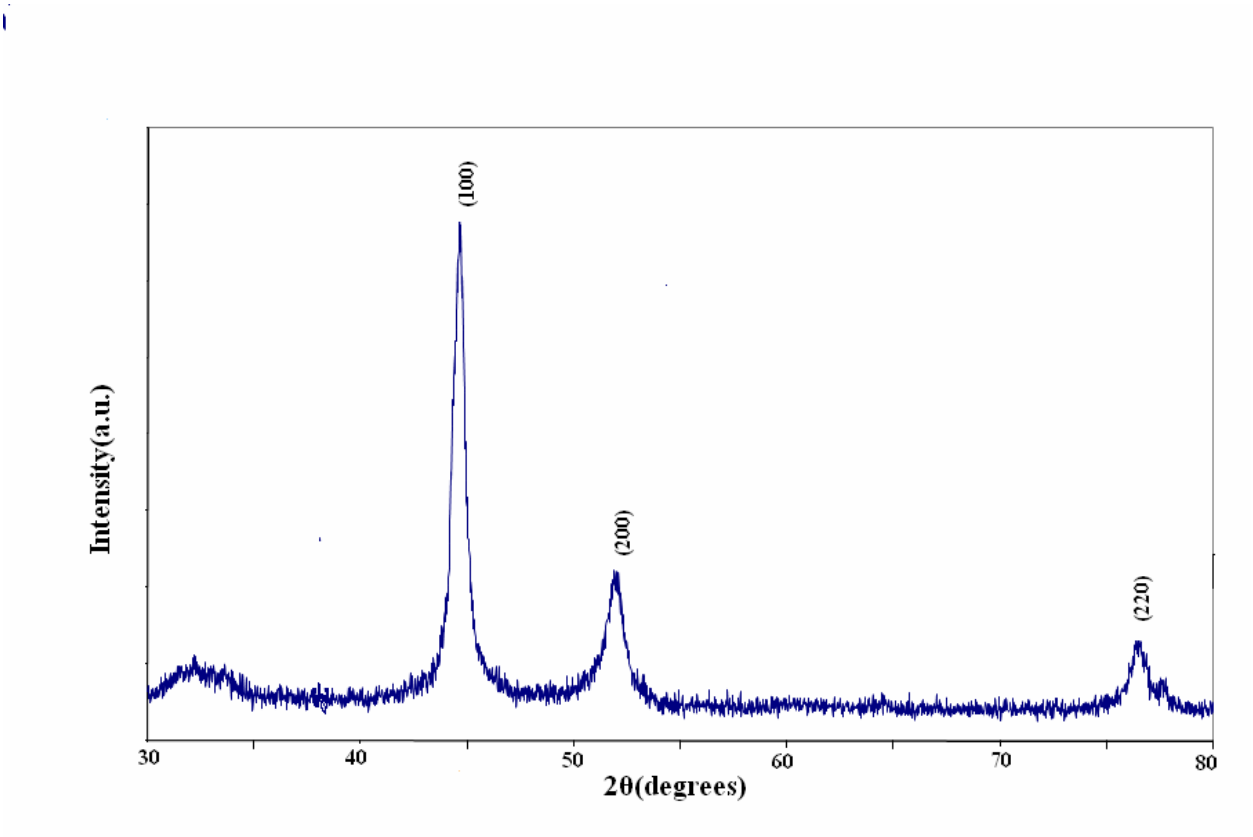


Fig. 4.3 *XRD pattern of NiCo alloy nanoparticles.*

The XRD of the composite (fig. 4.3) shows the characteristics peaks of NiCo particles along with the broad hump of PANI. Therefore this result shows the presence of nanoparticles in the PANI/NiCo composite. The XRD diffraction peaks of PANI/NiCo composite were found to shift to lower 2θ values as compared to the NiCo nanoparticles fig.4.2. The peak at 44.5˚ of NiCo is shifted to 43.5˚ and peak at 51.7˚ is shifted to 50.8˚. The peak shifting to lower angle in PANI/NiCo composite than the NiCo particles indicates the tensile stress in the composite. It might be attributed to the attachement of the nanoparticles with polymer chains.

The major shift is in the peak which is at 76.4˚in NiCo nanaoparticles, it is shifted to 72.58˚in the PANI/NiCo composite. The intensity also get modified in the composite. This peak is corresponding to the reflection from the [531] plane [48]. This peak may be explained on the basis of the attachment of the polymer chains of PANI with the NiCo particles. The polymer chains during the interaction may attach to the nanoparticles along this plane. This will increase the reflection intensity of the light.

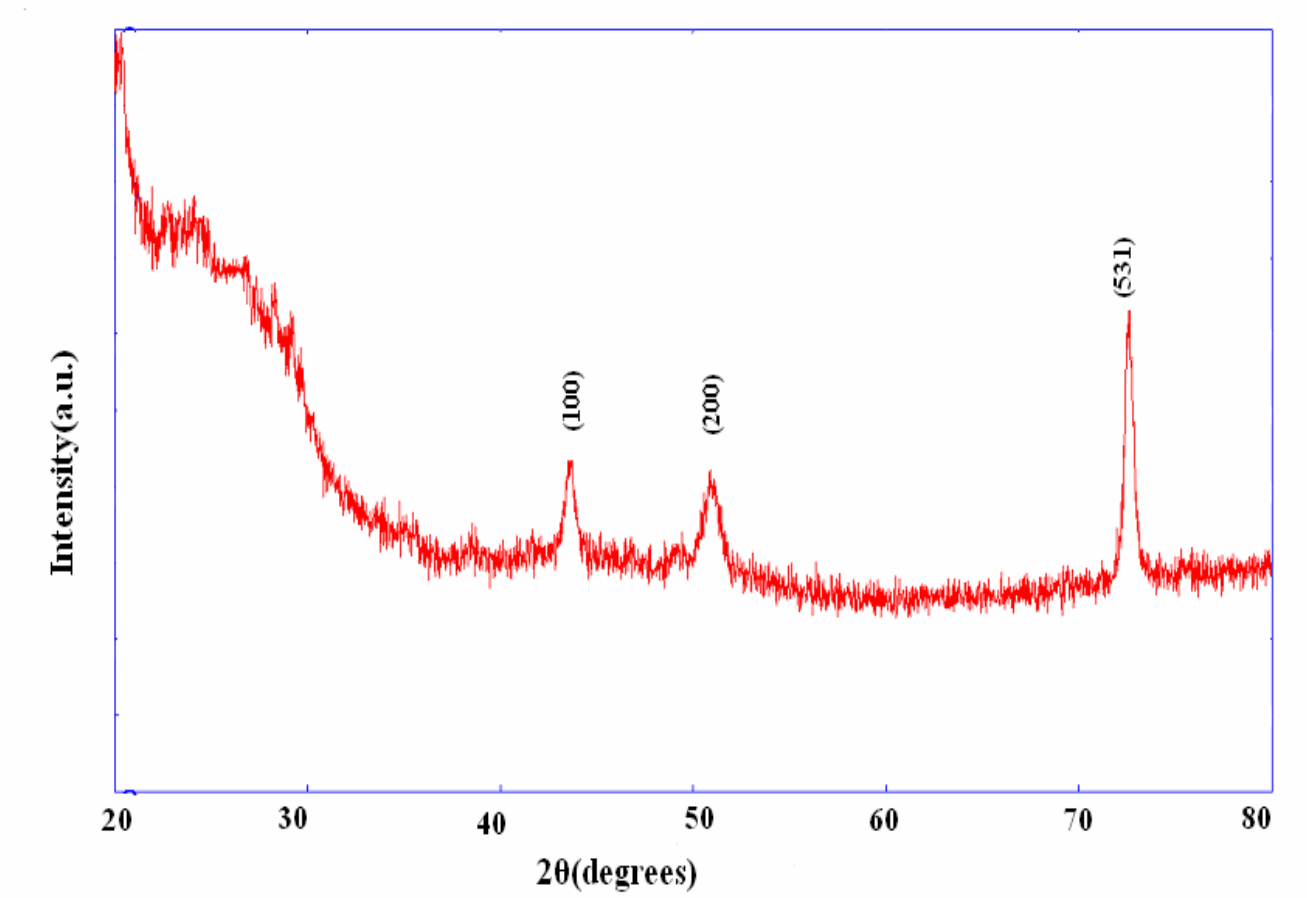


Fig. 4.4 *XRD pattern of PANI/NiCo composite.*

4.4 TGA ANALYSIS

The TGA- DSC studies were carried out in N_2 atmosphere from temperature 30^0C to 1000^0C at a ramp rate 10^0C/min. The thermal studies were carried out for PANI, PANI/NiCo composite and NiCo nanoparticles. The TGA curve of PANI shows 97% weight loss upto 190^0 as shown in fig.4.4. This loss in weight is attributed to the evaporation of the solvent. Furthermore, the TGA curve of PANI exhibits very less weight loss between 450^0 C to 600^0C. This is mainly contributed due to degradation of the polymer.

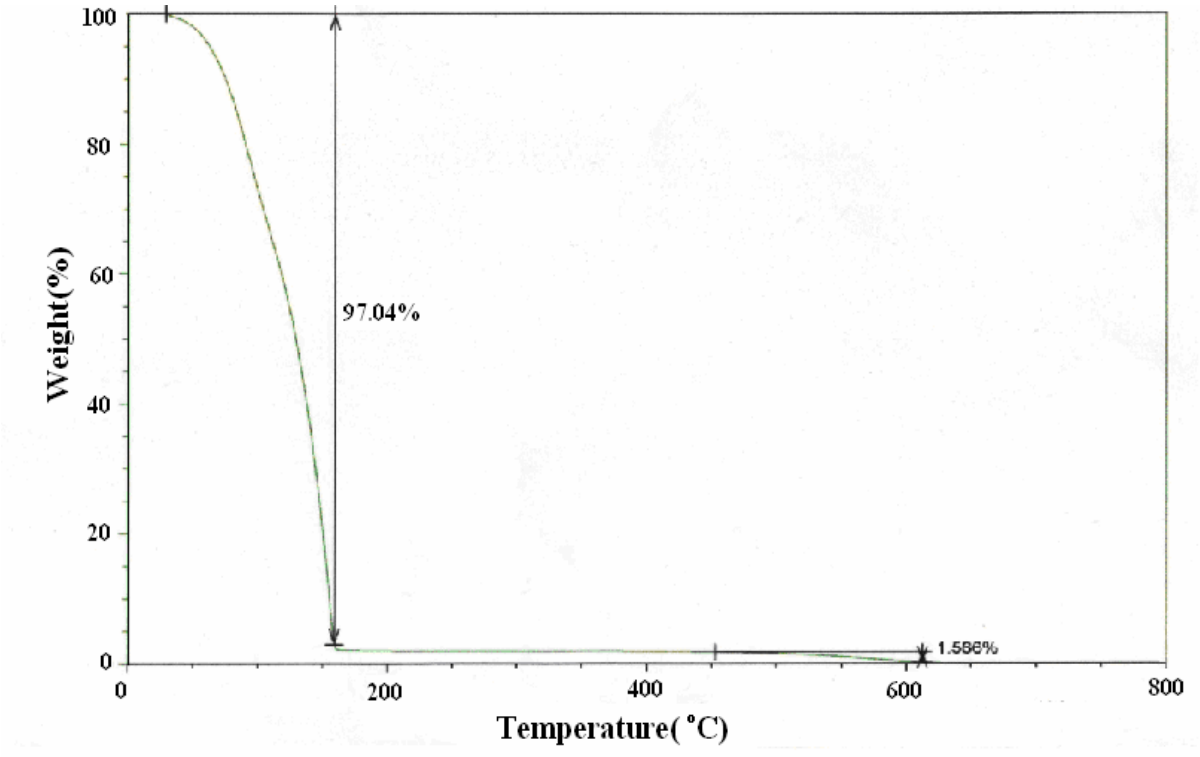


Fig. 4.5 *TGA of PANI*

The NiCo nanoparticles show weight loss 5% up to temperature 100^0C. This may be attributed to the moisture and water molecules molecules [49]. 6 % weight loss is observed upto 400^0C due to the degradation of capping agent . After it the weight loss becomes very slow up to 800^0C. in this temperature range the NiCo nanoparticles exhibit good thermal stability.

The TGA graph for composite is shown in the fig. 4.6. The graph can be divided into three parts. In fist part there is 65.79% weight loss which is due to solvent and due to s weight loss of capping agent (PVP). In second region about 17% weight is lost by the sample upto temperature 600^0C. This region is attributed to the weight loss due to PANI (as it is clear from the fig. 4.4). The third portion of TGA curve does not show appreciable change in weight of sample.

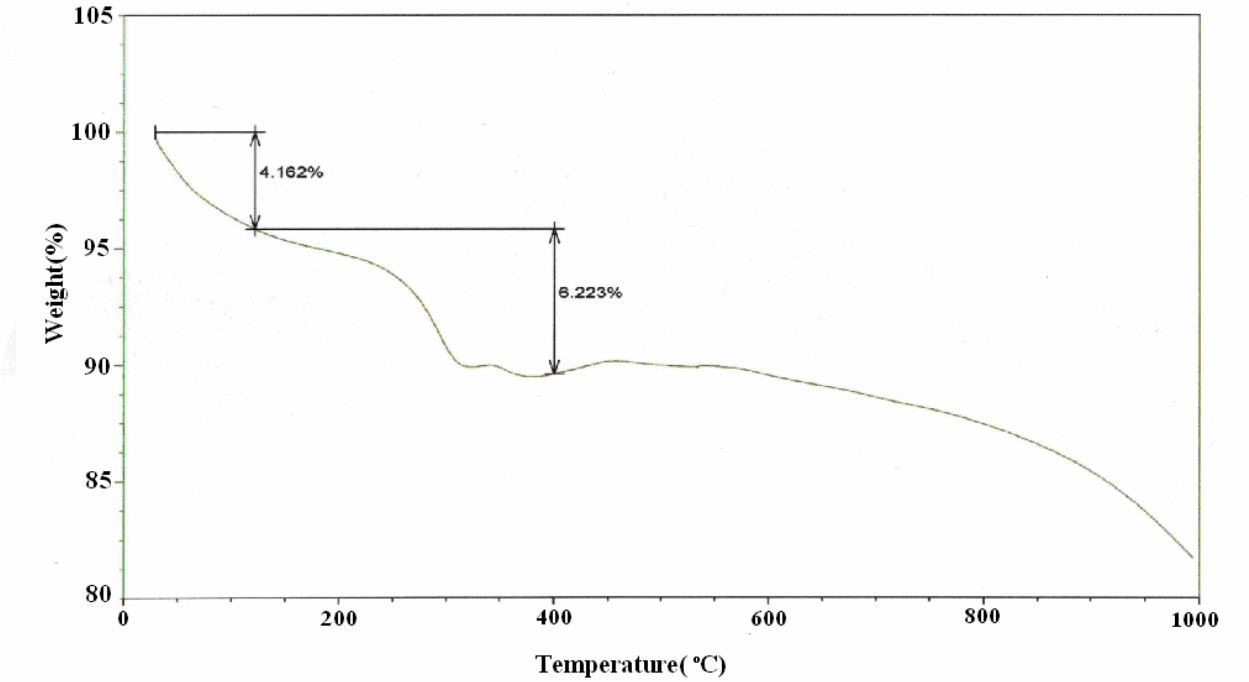


Fig.4.6 *TGA of NiCo nanoparticles*

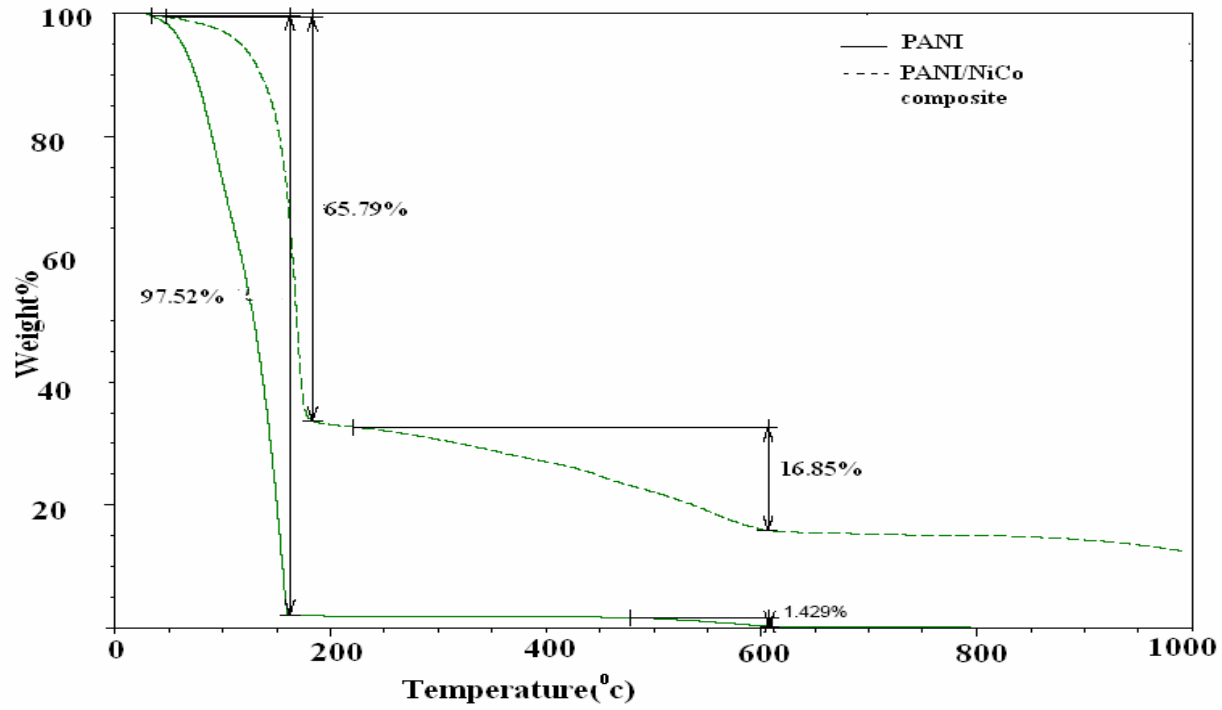


Fig.4.7 *TGA of PANI/ NiCo composite*

4.5 TRANSMISSION ELECTRON MICROSCOPE (TEM) ANALYSIS

The transmission microscope micrographs were taken for the NiCo nanoparticles and the composite of PANI/NiCo as shown in fig.4.7 and 4.8 respectively.

It is seen in the fig. 4.7 that the particles of nico alloy are nearly spherical. The average size of the nana particles is between 9-12 nm. The particle size of NiCo alloy nanoparticles is also observed approximately equal to 12 nm which is calculated from the XRD. The TEM images of the composite are shown in the fig.4.8 at different magnification. It is clear that the nanoparticles are attached to the polymer molecules as clearly indicated by the fig. 4.8.. In the image the dark portion which is spherical in nature are the nanoparticles and the gray areas is showing the polymer chain. Hence it is clear from the two micrographs that the polymer molecules have been adsorbed on the surface of the nanoparticles. The molecules of the PANI and the particles are hence bonded by weak bonds and they are formed the composite.

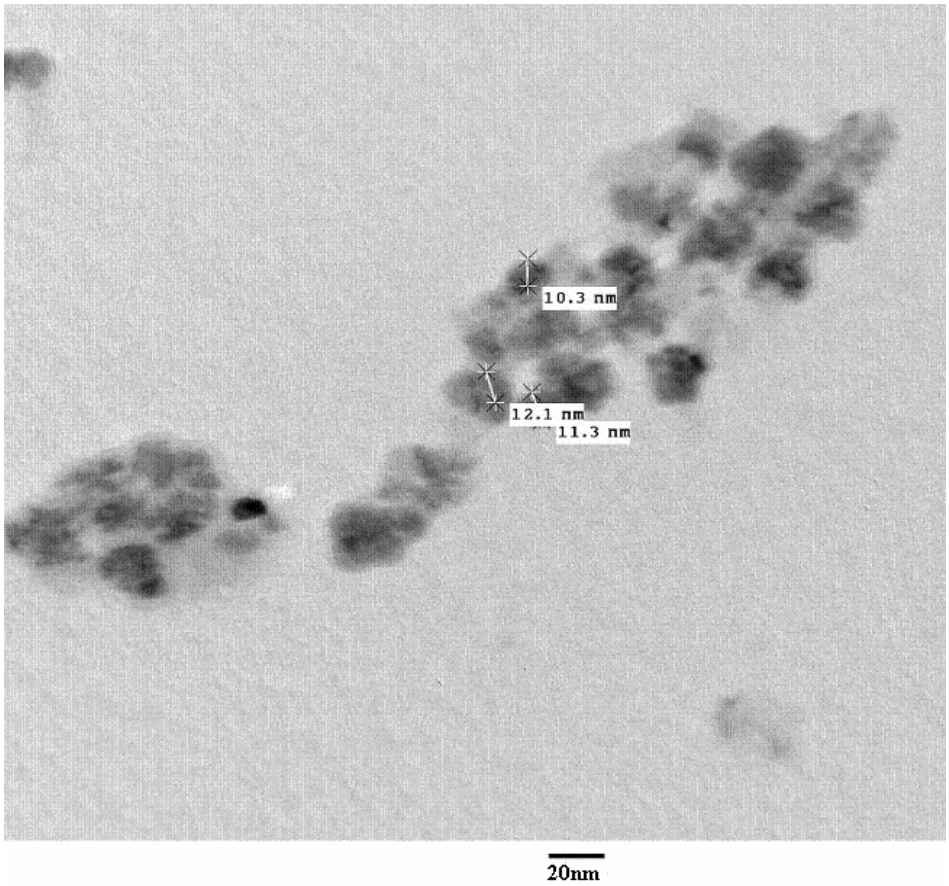


Fig. 4.8 *TEM image of NiCo nanoparticles.*

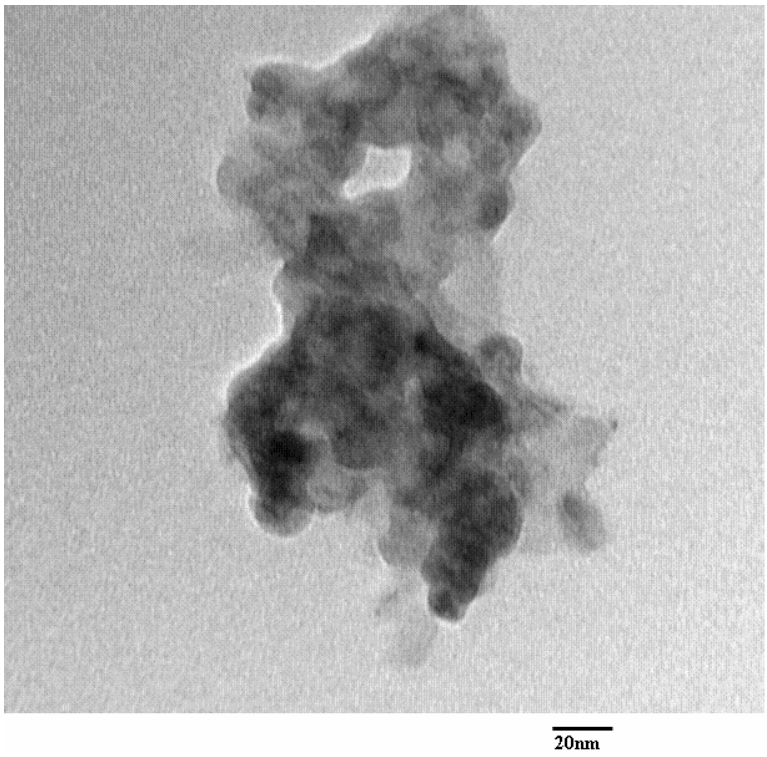


Fig. 4.9 *TEM micrographs of PANI/NiCo composite at different magnification*

4.6 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

The FTIR spectra of the pure PANI and the composite materials are shown in the fig. 4.9and 4.10 respectively. The two peaks at 3446.6 and 2369.3 cm^{-1} are due to the N-H stretching and C=N stretching. The FTIR spectra of pure PANI shows the peaks at 1559 cm^{-1} and 1472 cm^{-1} are attributed to the stretching vibrations of N=Q=N ring and N–B–N ring respectively. The peak at 1296 cm^{-1} orresponds to C–N stretching vibration. The peaks at 1121 and 798 cm^{-1} can be assigned to bands characteristic of B–NH–Q or B–NH–B bonds, and out-of-plane bending vibration of C–H of benzene rings (where B refers to the benzene-type rings and Q refers to the quinonic-type ring [50,51].

The FTIR spectra of the PANI/NiCo composite are shown in the fig. (4.10). FTIR spectra of composite shows more peaks than the polymer sample. The peaks which are corresponding to polyaniline are shifted towards higher wave number. The peak at 1559, 1472, 1296, 1128, and 798 cm^{-1} are shifted to 1560, 1499, 1304, 1126and 837cm^{-1} respectively. This may be due to the interaction between the polymer and the nanoparticles. And the peaks at position 1691, 1591 and 1021 cm^{-1} position are attributed to the C=0 and C-O stretching which is the functional group of the solvent cyclohexanone. Apart from these there are two peaks corresponding to 1120 and 966 cm^{-1}. These two peaks are due to C-H out of plane deformation (benzene ring) and C-H out of plane deformation. It means that during interaction between NiCo particles there is deformation of the bonds of the polymer molecules.

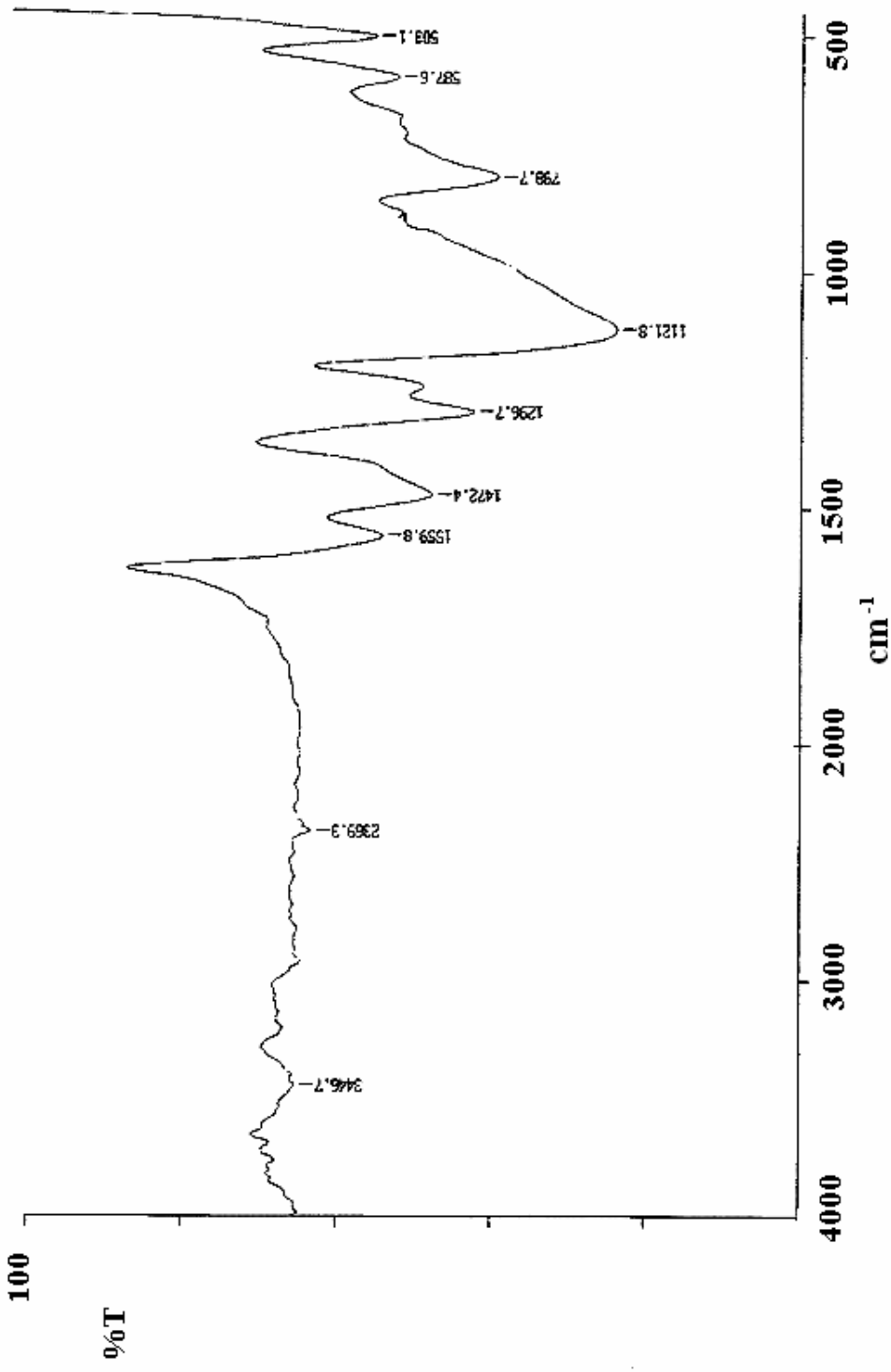


Fig.4.10 *FTIR of PANI*

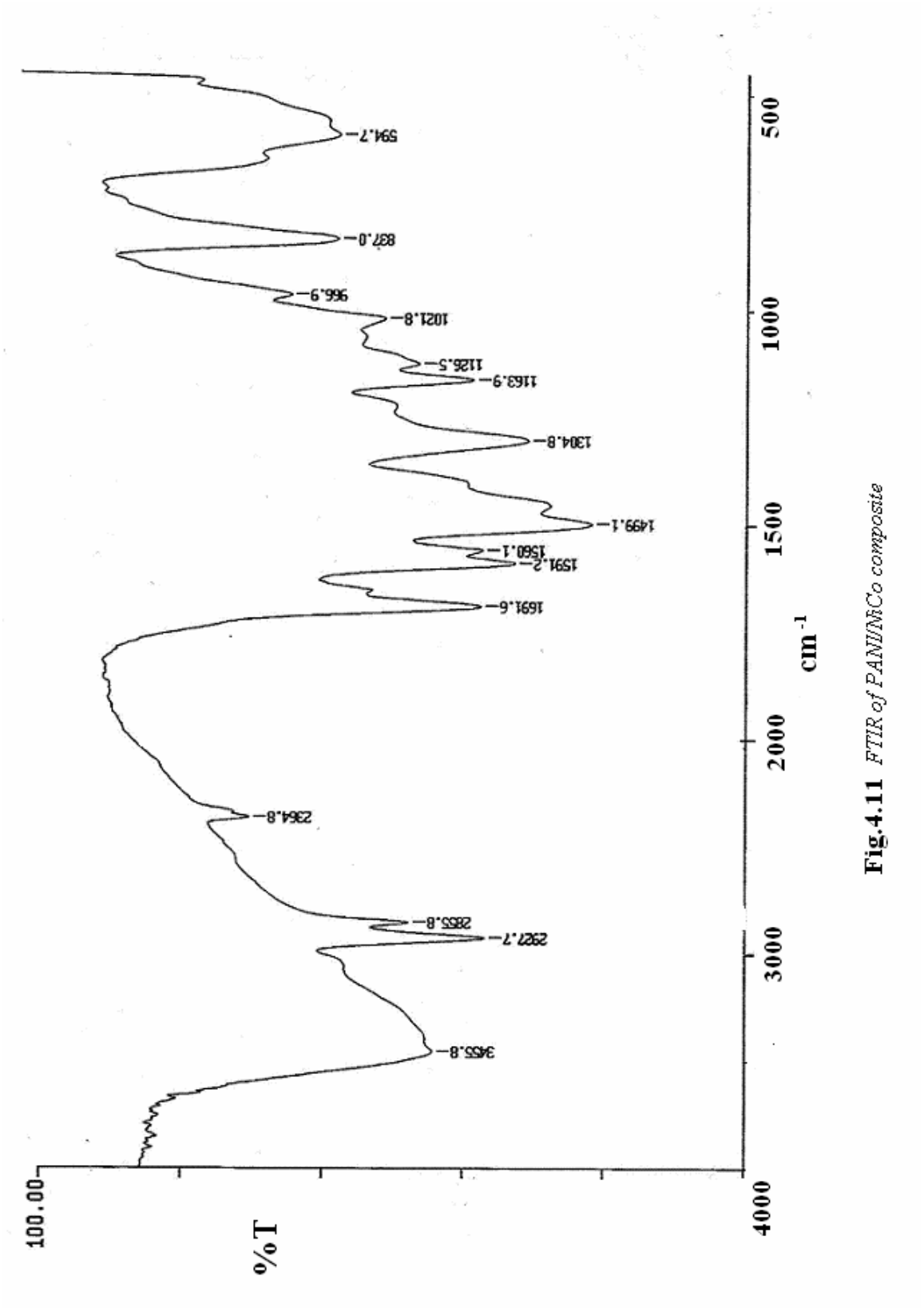


Fig.4.11 *FTIR of PANI/NiCo composite*

4.7 I-V CHAPACTERSTICS OF PANI AND PANI/NiCo COMPOSITE

I-V characteristics of the thin films of PANI and PANI/NiCo composites were observed to find the value of resistance for the films. I-V curve shown in the fig. 4.12 and 4.13. The resistance of the PANI film came out greater than the composite thin film. From the resistance value we can easily calculate the conductivity of the thin films. The conductivity of PANI/NiCo composite is one order higher than PANI polymers. Obviously it can be explained on the basis of change of ordering of the sample. The conductivities of both the samples are given in the table.

Table 6 *Conductivities of PANI and PANI/NiCo samples*

Sample name	Length of the thin film(cm)	Cross sectional area(cm^2)	R (Ω)	σ (S/cm)
PANI	1.2	1.107	1.574×10^{5}Ω	6.8×10^{-2}
PANI/NiCo	1.2	1.107	3.428×10^{4}Ω	3.1×10^{-1}

The enhancement of the conductivity in the composite is possible due to addition of metallic nanoparticles in the polymer. It has been also reported in the literature [52]. From the I-V characteristics it is clear that the current is not flowing uniformly through the thin film. In real systems, there are trapped charges near the nanoparticles which would lead to a random offset charge disorder. In the presence of such disorder, current does not flow uniformly through the nanoparticles film. In fact it is possible that there may be a few energetically favorable paths that carry most of the current [53, 54].

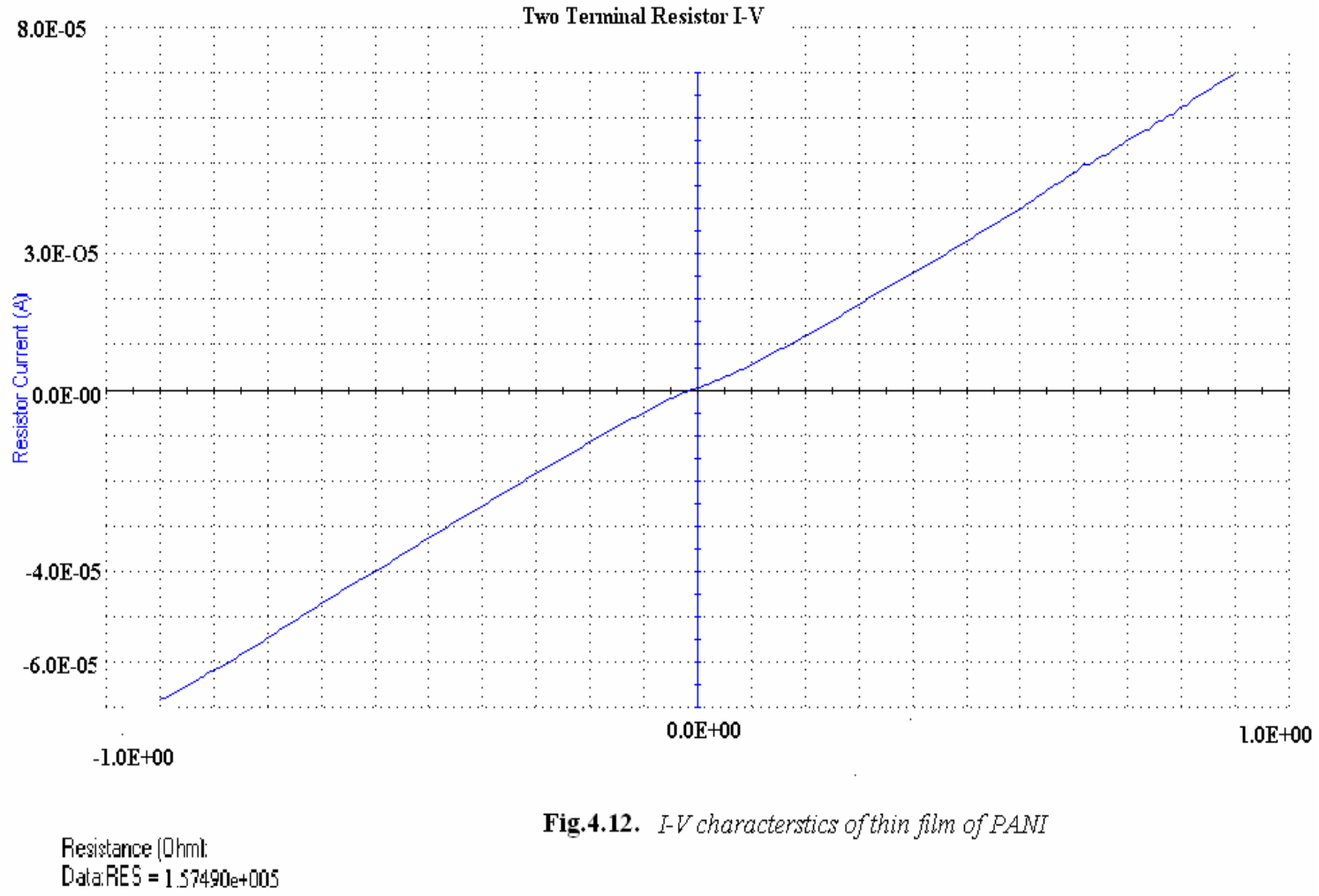


Fig.4.12. *I-V characterstics of thin film of PANI*

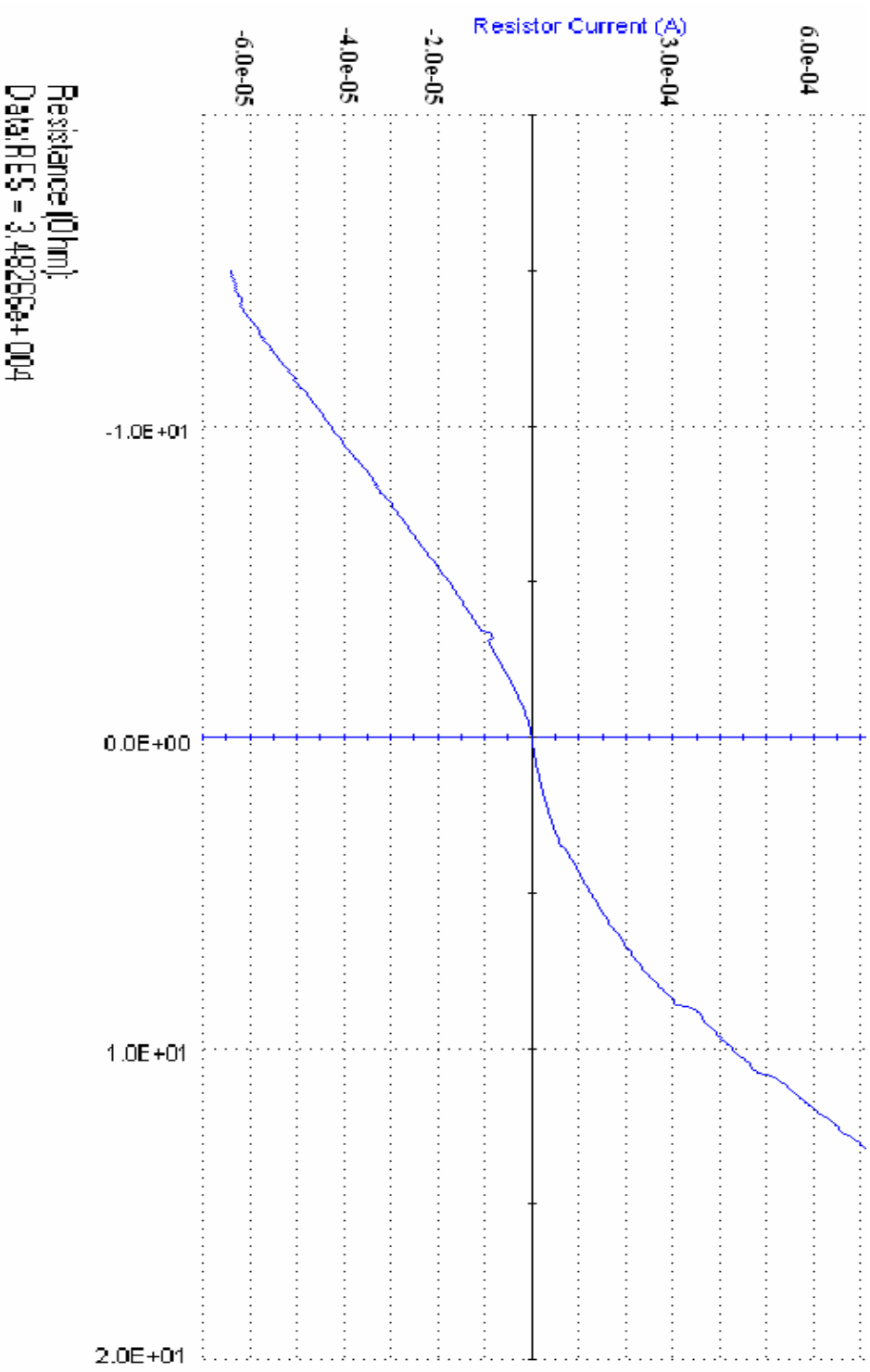


Fig.4.13. *I-V characteristics of thin film of PANI/MCo composite*

CHAPTER5

CONCLUSION AND FUTURE SCOPE

A brief conclusion which can be derived from the thesis is presented in this chapter. The future applications and the challenges which may be arising in the practical applications of the synthesized product is also discussed.

CHAPTER5
CONCLUSION AND FUTURE SCOPE

CONCLUSION

The thin films of PANI and PANI/NiCo composite are synthesized by simple spin coating method. The thickness of the film was measured to be 1.107µm. The composite PANI/NiCo exihibits higher conductivity than the PANI. Composite shows the attachment of the nanoparticles with the polymer chains. In FTIR spectra the peaks corresponding to the PANI are shifted to higher wave no. side, which again indicates the interaction between polymer chains and NiCo nanoparticles. The TGA study shows the greater thermal stability of the PANI/NiCo composite as compared to PANI alone. The XRD pattern also shows the attachment of the NiCo nanoparticles with the polymer chains.

FUTURE SCOPES

There are a lot of scopes to improve the stability of conducting polymers. Apart from this the synthesis should be simplified and cost effective. Electrical conductivity of these materials could be improved further by reducing defects in the long polymer chains that carry the current. The addition of the nanoparticles in the polyaniline may be carried out to synthesis the suitable product to use in various fields of engineering. Moreover the study of the mechanical properties of the present composite (PANI/NiCo) will provide the better understanding of the properties of the composite.

REFERENCES

[1] Bhavana A. Deore and Michael S. Freund,Macromolecules, 42 (1), 164-168 (2009).

[2] Manju Gerard, Asha Chaubey , B.D. Malhotra Biosensors & Bioelectronics 345–359 17 (2002).

[3] Md. Aminur Rahman, Pankaj Kumar, Deog-Su Park and Yoon-Bo Shim, Sensors, 8, 118-141 (2008).

[4] Komsiyska, V. tsakova, G. staikov, Appl. Phys. A 87, 405–409 (2007).

[5] Inzelt,G. "Conducting Polymers", chapter 8, 265-269 (2008).

[6] Herbert Naarmann “Polymers, Electrically Conducting” Ullmann's Encyclopedia of Industrial Chemistry Wiley-VCH, (2002)

[7] W. A. Little, Phys. Rev. 134,A1416 (1964).

[8] B A Bolto, R McNeill and DE Weiss, Australian Journal of Chemistry 16(6) 1090 (1963).

[9] R McNeill, D E Weiss and D. Willis ,Australian Journal of Chemistry 47718 (1965).

[10] McGinness, J.E., Corry, P.M., and Proctor, Science 183:853-855, (1974).

[11] J.P. Travers J. Chim. Phys. 95. 1427-1432(1998).

[12] Colin Pratt “ Conducting Polymers” (1996).

[13] Michael S.Fruend AND Bhavana Deore Canada “Self doped conducting polymers” John Wiley and sons 12,13 (2007).

[14] Yanzhe Wu, Amy M. Ballantyne , Pawel Wagner, Dezhi Zhoua,Geoffrey M. Spinks, David Officer , Gordon G. Wallace, Electrochimica Acta 53 1830–1836(2007).

[15] Lars Herlogsson, Xavier Crispin, Nathaniel D. Robinson, Mats Sandberg, Olle-Jonny Hagel, Göran Gustafsson, and Magnus Berggre DOI: 10.1002/adma.200600871

[16] V. V. Erokhin , T. S. Berzina and M. P. Fontana, ISSN 1063-7745, Crystallography Reports, Vol. 52, No. 1, pp. 159–166 (2007).

[17] Matthew J. Panzer and C. Daniel Frisbie. J. Am. Chem. Soc ,129(20),6599-6607 (2007).

[18] Tunç Tüken , Birgül Yazici, Mehmet Erbil ,Surface & Coatings Technology 425–432, 202 (2007).

[19] J. STEJSKAL, R. G. GILBERT Pure Appl. Chem., Vol. 74, No. 5, pp. 857–867, (2002).

[20] Spectroscopic observation of polaron-lattice band structure in the conducting polymer polyaniline ens. Matter 13 3907-391.

[21] Z Kurmaev et al 2001 J. Phys.: Cond 1. R. Gangopadhyay, A. De, Chem. Mater.12, 608 (2000).

[22] Z. Peng, L. Guo, Z. Zhang, B. Tesche, T. Wilke, D. Ogermann, S. Hu, K. Kleinermanns,Langmuir 22, 10915 (2006)

[23] Matsunaga et al 1990; Gustafsson et al 1992; Olcani et al 1993.

[24] Yuvraj Singh Negi and P. V. Adhyapak ,Polymer Research and Development Division, Centre for Materials for Electronics Technology, 42, 35-53.

[25] Rosa Vera a, Hugo romero,Eduardo ahumada, J. Chil. Chem. Soc. v.48 (2003).

[26] M. Sacak, M.Karakisla, E.Erdem and U. Akbulut, Journal of Applied Electrochemistry, 309-316,27 (1997).

[27] S. Bekir and M.Talu, Turk J Chem, 22,301-307(1998).

[28] Mir Reza Majidi, Leon A. P. Kane-Maguire and Gordon G. Wallace Australian Journal of Chemistry, 5 (1), 23–30.

[29] Y.-N. Qi, F. Xu1, H.-J. Ma, L.-X. Sun1, J. Zhang, and T. Jiang.Journal of Thermal Analysis and Calorimetry, 219–223, Vol.1 91 (2008) .

[30] Pilli Satyananda Kishore, Balasubramanian Viswanathan, Thirukkallam Kanthadai Varadarajan Nanoscale Res Lett 3:14–20 DOI 10.1007/s11671-007-9107-z (2008).

[31] R. Del RIÂO, J.H. ZAGAL, G.de T. ANDRADE and S.R. BIAGGIO Journal of Applied Electrochemistry 29: 759-764, (1999).

[32] Nirmalya Ballav, Mukul Biswas, Materials Letters 60 514–517 (2006).

[33] Hu Yan, Kazuhisa Tomizawa, Hiroyuki Ohno, Naoki Toshima, Macromol. Mater. Eng.288, 578–584,(2003).

[34] Jaczewska, A. Budkowski, A. Bernasik, I. Raptis, J. Raczkowska, D. Goustouridis,J. Rysz, M. Sanopoulou DOI 10.1002/app.26012, (2006).

[35] X H Xia, J P Tu, J Zhang, X L Wang, W K Zhang and H Huang ,Nanotechnology 19 465701, 7(pp) (2008).

[36] Chris E. Scott Associate Professor of Polymer Engineering Department of Materials Science and Engineering Massachusetts Institute of Technology, Feature Article Dec.(2000).

[37] Champness, P. E. (2001). Electron Diffraction in the Transmission Electron Microscope. Garland Science.

[38] L.E. Alexander, "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials", Wiley, New York, (1954).

[39] L. E. Alexander, X-ray Diffraction in Polymer Science", Wiley, London, (1969).

[40] P. C. Painter, M. M. Coleman, J. L. Koenig, "The Theory of Vibrational Spectroscopy and its Application to the Polymeric Materials", John Wiley & Sons,Chichester, (1982).

[41] J. L. Koenig, "Spectroscopy of Polymers", Elsevier, Amsterdam, (1999).

[42] V.A. Bershtien, "Differential Scanning Calorimetry of Polymers", Ellis Horwood, Chichester, 1994.

[43] Electron Microscopy and Analysis by : P.J. Goodhew, University of Surrey and F.J. Humphreys, UK Imperial College, London,UK.

[44] Hiklová Helenaa, Havelková Martinaa ,MEASURING CAPABILITIES OF FORM TALYSURF SERIES 2 INSTRUMENT Joint laboratory of Optics of Palacky University and Institute of Physics of Academy of Sciences of the Czech Republic.

[45] Manish kumar, M.L Singla.

[46] Yavuz O., Ram M. K., Aldissi M., Poddar P., Harihara:. Journal of Materials Chemistry, 15,810–817(2005).

[47] D.H. Chen, C.H. Hsieh, J. Mater. Chem. 2412. 12 (2002).

[48] ICDD (international standard for diffraction data) card no. 01-1258.

[49] Syukri, Takayuki Ban, Yutaka Ohya, Yasutaka Takahashi Materials Chemistry and Physics 78,645–649 (2003)

[50] Laska J., Widlarz J,Polymer, 46, 1485–1495 (2005).

[51] Zeng X-R., Ko T-M, Part B: Polymer Physics, 35, 1993– 2001 (1997).

[52] Z. Peng, L. Guo, Z. Zhang, B. Tesche, T. Wilke, D. Ogermann, S. Hu, K. Kleinermanns, Langmuir 22, 10915 (2006).

[53] C. Reichhardt and C.J. Olson Reichhardt, *Phys. Rev. Lett.*, **90**, (2002), 046802.

[54] A. Alan Middleton and Ned S. Wingreen, *Phys. Rev. Lett.*, **71**, (1993), 3198.