Chapter 2
Synthesis Methods of Polyaniline Based Composites

Muktikanta Panigrahi [1], *, Basudam Adhikari [1]

[1] Materials Science Centre, Indian Institute of Technology, Kharagpur, West Bengal, India

*Corresponding author: muktikanta2@gmail.com

Abstract

Polymer composites synthesized in the present work have been studied extensively. Polymer composites are investigated using sophisticated analytical tools. Electron microscopy was used to study the surface morphology by SEM/FESEM and dispersion of nanoparticles in the polymer matrix by HRTEM. The structural details, i.e., crystallite size, crystallinity, types of nano structure were studied by X-ray diffraction. H1-NMR, ESI-MS and FTIR have been used to elucidate chemical structure of synthesised monomers. The conformational variations in the polymeric materials have been studied using vibrational spectroscopy employing Fourier Transform Infrared (FTIR) spectroscopy. The UV-Visible absorption spectroscopy was used to study the optical properties of the monomers, and as-prepared polymeric samples. The DC conductivity measurement was carried out to study the electronic properties and charge transport mechanisms of the prepared polymeric samples. The gas sensing response was found by electrical measurement. Thermal study has been used to study the stability of prepared materials.

Introduction

The fundamental requisite in the synthesis of conducting polymers is the conjugated nature of the monomer. That is conserved the synthesis process of conducting polymer. Choices of monomer and polymerization method are two main parameters for synthesizing conducting polymer. It is great difficult to synthesize conducting polymer from monomers. Also, there is great challenge to develop a polymerization process by considering appropriate functionality of monomer(s). Generally, most of the monomers are electron-rich molecules. Some of contains simple electron rich molecules *i.e.,* acetylene and other some molecules contains electron rich molecules with pendant groups *i.e.,* aniline, pyrrole, thiophene, or 3,4-ethylenedioxythiophenes. Polymerization reaction occurred of a given monomer in

many routes. Numerous methods are used to polymerize the given monomer. Both monomer and polymer in polymerization reactions are completely soluble and there is possibility for forming high molecular weight polymer. There are two principal methods for the synthesis of PANI. The first one is the direct oxidation of aniline by chemical oxidation, *i.e.,* chemical method and the second way is through electro-oxidation on an inert electrode, *i.e.,* electrochemical method and is discussed below;

Chemical Synthesis

PANI-ES can be easily obtained as dark green powder by polymerization of aniline in aqueous acid medium using ammonium persulfate (APS) oxidant [**1** 10], potassium iodate [**2** 14], hydrogen peroxide [**3** 15], potassium dichromate [**4** 16], etc. The possible polymerization routes and availability of list of oxidant is shown in **Table** 1. The reaction is mainly carried out in acid medium at low pH (pH ~ 0 and 2). The concentration of the monomer used varies from 0.01 to 1 M. Generally, a stoichiometric equivalent of oxidant is used to carry the polymerisation and also to avoid degradation of the polymer [**5** 17]. Chemical oxidation polymerization is generally carried out at low temperature (−5 to 0 °C) in order to achieve high molecular weight PANI. One of the disadvantages of this method stems from the experimental observation that an excess of the oxidant and higher ionic strength of the acid medium leads to materials that are essentially intractable.

In a typical synthesis of PANI Emeraldine salt (ES), aniline (0.1 M) is dissolved in 1 M solution of protonic acid such as HCl, H_2SO_4, $HClO_4$, etc. and is cooled to 0–5 °C. A precooled solution of oxidant (0.1 M) with or without protonic acid is added drop wise for 30-60 min. After about 10-15 min, the solution gradually develops a green tint. The dark green/blue-green precipitate (ES) formed after 12 h and then it is filtered, washed with excess of dilute acid and then with organic solvents. After that the products are dried in vacuum for 24 h. Emeraldine salt (ES) form of PANI can be obtained. PANI Emeraldine base (EB) can be obtained by stirring PANI-ES powder in 0.05 M solution of NH_4OH for 10-12 h. The dark blue powder of EB is further washed with 0.05 M NH_4OH and dried under vacuum. Other than the chemical oxidation method [**1** 10], emulsion polymerization [**6** 18], dispersion polymerization [**7** 19], interfacial polymerization [**8** 20], and etc. are also available for the polymerization of aniline. The possible polymerization routes and availability of list of oxidants have been thoroughly reviewed in the literature mentioned in **Table** 1.

Electrochemical Synthesis

In this route, polymerization of aniline is carried out in a three electrode system to produce good yield of PANI. The anodic oxidation of aniline is generally carried out on an inert electrode material which is usually platinum (counter electrode). However, other electrode materials such as iron, copper are employed as working electrode [**9** 21], whereas Ag/AgCl electrode is used as reference electrode. Homogeneous polymer is obtained when synthesized *via* potential cycling [9 21]. The

anodic oxidation of aniline is normally carried out in an inert atmosphere at ambient temperature. For many conceivable applications, deposition of the PANI as a thin film or thick coating is desirable which can be easily achieved using electrochemical polymerization.

Table 1. Types of polymerisation processes, oxidants and dopants

| Types of Conducting polymers	Pol merization process	Types of Oxidant	Dopants	Reference
PANI-ES	Chemical-oxidation	APS	HCl	[**1** 10]
PANI- S	hemical-oxidation	APS	AA	[**10** 22]
PANI-ES	Chem ca - oxidation	APS FeCl$_3$ CuCl$_2$	---	[**11** 23]
PANI-ES	Emulsion route	APS	HCl	[**6** 18]
PANI-ES	Inverse emulsion	APS	DBSA	[**12** 24]
PANI-ES	Electrochemical	---	HClO$_4$	[**13** 25]
PANI-ES	Electrochemical	---	HCl	[**9** 21]
PANI-ES	Electrochemical	---	HNO$_3$	[**14** 26]

Polymerization of aniline

The mechanism and kinetics of PANI formation have been extensively studied for the identification of intermediates and steps involved [**15** 27]. Various polymerization mechanisms and electrochemical aspects of the formation of PANI have been proposed by different authors depending on the protocol used in the synthesis of PANI [**15, 16** 27,28]. The first step in the reaction is the formation of a radical cation which is resonance stabilized by several canonical forms (Scheme 1)
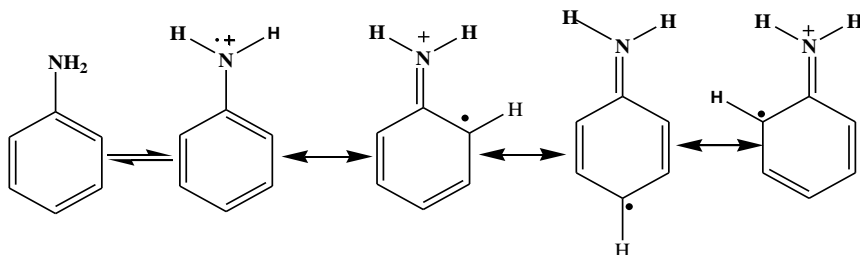
Scheme 1. Formation of radical cation and its resonance stabilized canonical forms

This dimer, further leads to higher intermediates and finally to emeraldine form (Scheme 2) [**17, 18** 29, 30].
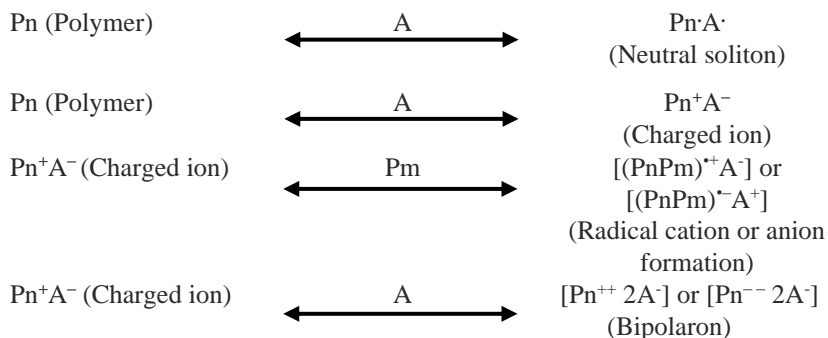
The polymerization mechanism is characterized as 'autocatalytic'. This may occur due to less positive potentials of the oligomers compared to aniline monomer. Such an autocatalytic effect is observed only in aqueous solutions with significant acidity [27].
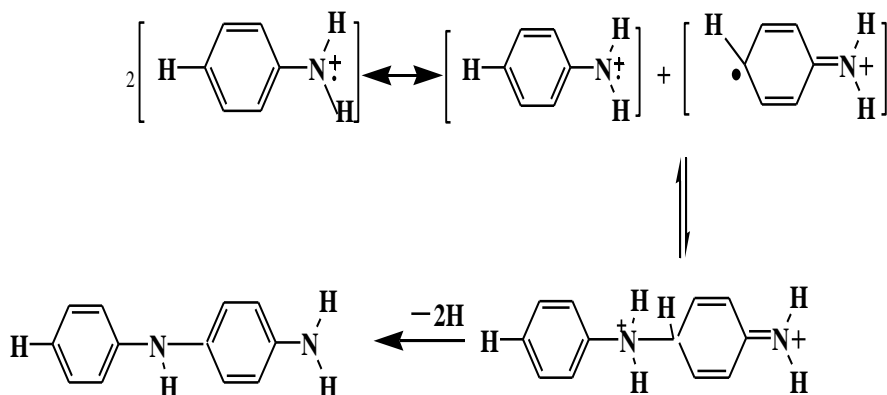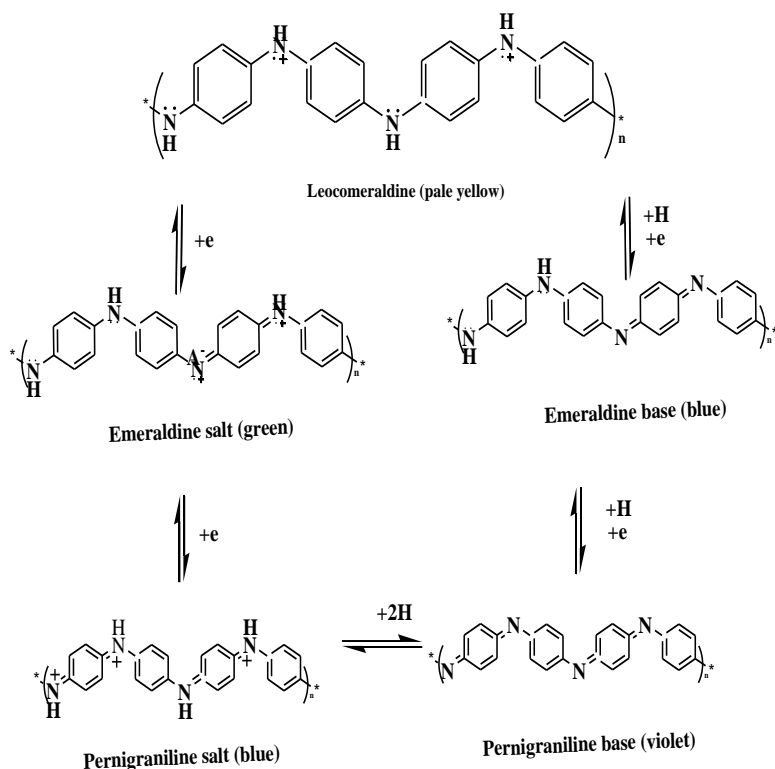

Scheme 1.3. Formation of p-amino diphenylamine from the monomeric radical cation

Doping in Polyaniline: Acid Doping

Usually, the conductivity of undoped state of the conjugated polymers is low (10^{-7}–10^{-11} S cm^{-1}) [**19** 3]. One of the effective ways to improve the conductivity is doping. When the conjugated polymers are doped, the electrical conductivity of the polymers increases to several folds [**19** 3]. Doping in most of the known conducting polymers is achieved by partial oxidation by electron donor or partial reduction by electron acceptor of the π-systems polymer which leads to either increase or decrease in the number of electrons associated with it [**20** 32]. Generally, doping process can occur either by electron donation or acceptance to the polymer by the dopant (donor) and the resultant species is known as neutral soliton [**1, 21** 10,33]. If both the electrons are accepted (cation) or donated (anion) by the dopant then the charged soliton is formed **1, 21** [10,33]. After the first redox process, charge transfer complex may form between the charged soliton and neutral segment of the polymer. As a result, radical cation or radical anion is formed, which is called polaron [**1, 21** 10, 33]. Alternatively, charged soliton formation may be followed by a second electron transfer with the dopant. This process results the formation of a dication or dianion, which is known as bipolaron [**21** 33]. Formation of soliton, polaron, bipolaron is shown in Scheme 3.

Pn (Polymer)	A	Pn·A·
		(Neutral soliton)
Pn (Polymer)	A	Pn^+A^-
		(Charged ion)
Pn^+A^- (Charged ion)	Pm	$[(PnPm)^{·+}A^-]$ or
		$[(PnPm)^{·-}A^+]$
		(Radical cation or anion
		formation)
Pn^+A^- (Charged ion)	A	$[Pn^{++} 2A^-]$ or $[Pn^{--} 2A^-]$
		(Bipolaron)

Scheme 3. Formation of soliton, polaron and bipolaron

Scheme 4. Interconversion of different oxidation states of polyaniline via redox procedure [22 34]

After doping, non-conducting form of PANI, *i.e.,* emeraldine base (EB) forms conducting PANI, *i.e.,* emeraldine salt (ES) [**22** 34]. Such a doping behaviour is achieved by the introduction of protonic acids (mineral or organic) and is known as 'acid doping' (Scheme 1.5). In this doping process, the conductivity of PANI increases

more than eight orders of magnitude [**23** 35]. Positive charges accumulated on the polymeric backbone during protonation of PANI are neutralized by the negatively charged counter ions of the dopant, called polymeric organic salts. The protonation changes the electronic structure, crystallinity, solubility, etc. of the polymer [**20** 32]. The degree of protonation and the conductivity can be controlled by changing the concentration of the dopant acid solution. Mineral acids such as HCl, H_2SO_4, etc are the most frequently used as dopants.

Limitation of conducting polymer

Though, the conducting polymer has potential application in the different fields as an optoelectronic material instead of inorganic materials, still, it has some limitations. The problems of conducting polymers are related to their synthesis, reproducibility, types of dopant used, processability, and stability. Among these problems, the processability and stability are most prominent.

Polymer nanocomposites

The emergence of polymer nanocomposites is largely based on a consideration in which polymer matrix is reinforced by uniformly dispersed nano-sized particles [**24, 25** 51,52]. Polymer nanocomposites can be prepared using a variety of nanomaterials including disk-like nanoparticles (*e.g.,* clay platelets), spherical and polyhedral nanoparticles (*e.g.,* colloidal silica) and nanofibers (*e.g.,* nanotubes, whiskers). There are many reports on polymer nanocomposites with improved properties other than individual components or their macro- and micro-counterpart [**24-26** 51-53].

Clay minerals

The layered clays which can be used for the preparation of polymer nanocomposites may be divided into two types. One is natural clays (*e.g.,* montmorillonite, hectorite and saponite etc.) and other one is synthesized clays (*e.g.,* fluorohectorite, laponite, mica, magadiite and hydrotalcite). These are presented in **Table 2.** Out of them, both MMT and hectorite are the most commonly used. The hydrotalcite clays are called anionic clay because the layered clay bears negative clay layers. Among the large amount of layered solids, clay minerals especially the members of smectite group are most suitable for the reinforcement of polymer matrix. For the fabrication of clay based polymer nanocomposites, clay materials are used because of their unique structure and high aspect ratio of each clay platelet. The basic structures of nanoclays are composed of layered silicate network. The silanol groups contains hydroxy group in the inter layer regions, which favour the organic modification by grafting organic functional groups in the interlayer regions (**Fig. 1**) [**24-26** 51-53].
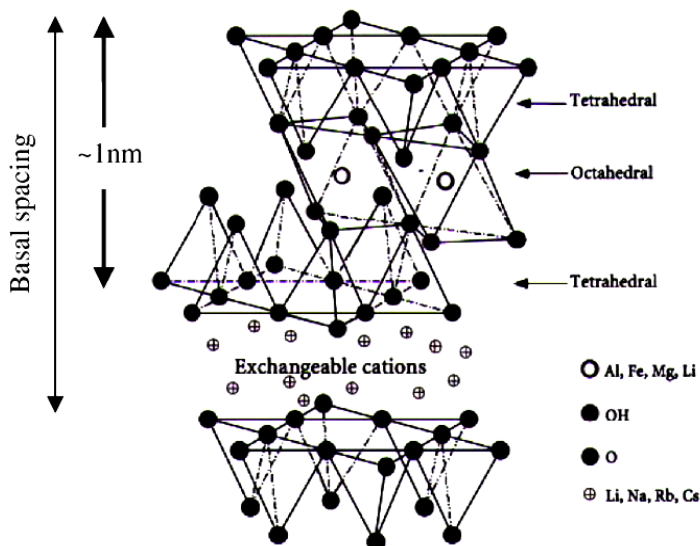
Figure 1. Schematic representation of the clay structure [24 51]

Table 2. Classification of nanoclays (Phallosilicate) [27, 28 54,55]

Type of clay	Formula	Origin	Substitution	Layer charge
2:1 type				
MMT	$M_x (Al_{2-x}Mg_xSi4O_{10}(OH)_2nH_2O$	N	Octahedral	-ve
Hectorite	$M_x (Mg_{3-x}Li_x) Si_4O_{10}(OH)_2nH_2O$	N	Octahedral	-ve
Saponite	$M_xMg_3(Si_{4-x}) Al_xO_{10}(OH)_2nH_2O$	N	Tetrahedral	-ve
Fluorohectorite	$Mx (Mg_{3-x}Li_x) Si_4O_{10}F_2nH_2O$	S	Octahedral	-ve
Laponite	$M_x (Mg_{3-x}Li_x) Si_4O_{10}(OH)_2nH_2O$	S	Octahedral	-ve
Fluoromica	$NaMg_{2.5}Si_4O_{10}F_2$	S	Octahedral	-ve
1:1 type				
Kaolinite	$Al_2Si_2O_5(OH)_4$	N	---	Neutral
Halloysite	$Al_2Si_2O_5(OH)_42H_2O$	N	---	Neutral
Hydrotalcite	$Mg_6Al_2(CO_3)(OH)_{16}4H_2O$	S	Octahedral	+ve
Layered silicic acid				
Kanemite	$NaHSi_2O_57H_2O$	N/S	Tetrahedral	-ve
Makatite	$Na_2Si_4O_9.5H_2O$	N/S	Tetrahedral	-ve
Octasilicate	$Na_2Si_8O_{17}.9H_2O$	S	Tetrahedral	-ve
Magadiite	$Na_2Si_{14}O_{29}10H_2O$	N/S	Tetrahedral	-ve
Kenyaite	$Na_2Si_{20}O_4.10H_2O$	N/S	Tetrahedral	-ve

M indicates exchangeable ions represented by monovalent ions. Symbols: N (Natural), S (Synthetic), -ve and +ve

Modification of clay minerals

Purification and surface modification is essential for the preparation of polymer nanocomposites. This is essential because of their hydrophilic and incompatible nature to most polymers. Therefore, the dispersion of clay minerals in polymer matrix is very difficult. Some parameters of MMT and organically modified nanoclays are presented in **Table 3**.

Table 3. Some parameters of MMT and organically modified nanoclays

OMLS code	Pristine Layered Silicate	d_{001} (nm)	CEC meq /100g	Modifying group name	Reference No.
MEE	Synthetic clay	2.2	120	Dipoly oxy ethylene alkyl methyl ammonium cation	**29** 56
MAE		3.3	120	Dimethyl dialkyl ammonium cation	**29** 56
ME100		0.95	120	Unmodified mica	**30** 57
30B	Southern clay (Natural clay)	1.85	90	Methyl, tallow,bis-2-hydroxyethyl quaternary ammonium chloride	**30** 57
15A		3.15	125	Dimethyl, dihydrogenated tallow quaternary ammonium chloride	**31** 58
20A		2.42	95	Dimethyl-2-dihydrogenated tallow, quaternary ammonium	**30** 57
25A		1.86	95	Dimethyl, dihydrogenated tallow, 2-ethylhexyl quaternary ammonium	**32** 59
93A		2.36	95	Dimethyl, dihydrogenated tallow, ammonium	**33** 60
NC		1.17	92	Unmodified MMT	**24** 51

*MMT indicates montmorillonite. **Abbreviation: OMLS** (Organically modifying layered silicate), **CEC** (Chemical exchange cation), **nm** (nano meter), **meq.** (Miliequivalent), and **d** (basal distance), and **NC** (Nanoclay which is unmodified)*

Conducting polymer nanocomposite

When clay minerals are added to a polymer matrix, they form three types of structures, which depend on the nature of the components and processing condition. These are conventional composite, intercalated, and exfoliated nanocomposites. In conventional composite, the components are separated, *i.e.*, phase separated. The properties of such composite are similar to that of micro-particles reinforced polymer composites. In intercalated nanocomposites, the polymer chain is inserted into the clay gallery resulting in a well ordered multilayer stacking morphology. **Fig. 2** shows a diagram of three broad classes of thermodynamically achievable polymer/layered silicate nanocomposites [**24** 51].
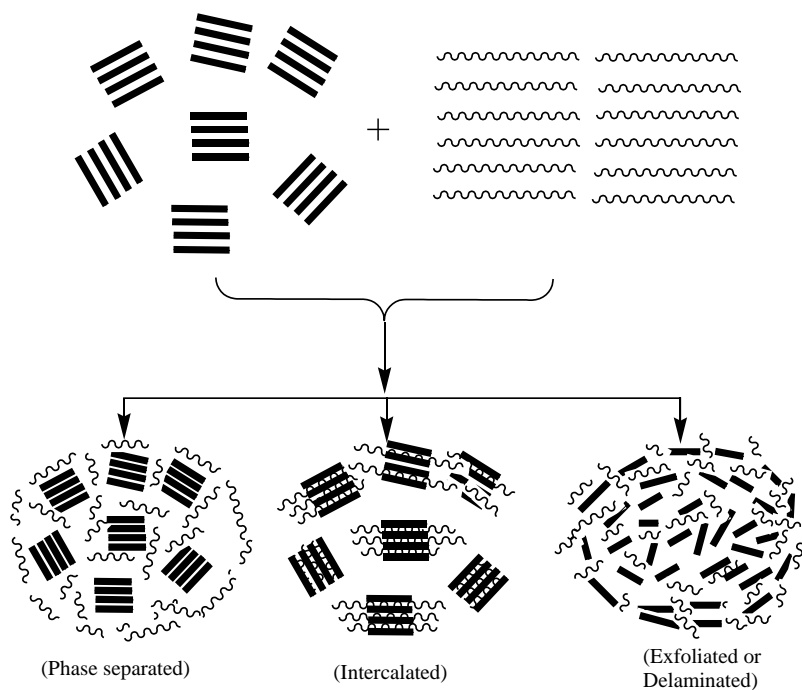

Figure 2. Three typical nanocomposites prepared from conducting polymer and clay minerals: (a) phase separated nanocomposite; (b) intercalated nanocomposite; (c) exfoliated or delaminated nanocomposite [24 51]

Several techniques are followed for the preparation of nanocomposites, which predominantly includes chemical and electrochemical techniques [**34** 61]. Nanomaterials are encapsulated in various ways *viz., ex situ*, *in situ, and core-shell*.

Ex situ nanocomposites

In *ex situ* technique the inorganic nanoparticles are dispersed in a monomer and then polymerised to form conducting polymer nanocomposites [**35** 62]. The

inorganic nanoparticles are encapsulated in the conducting polymer matrix during polymerization in the same reaction vessel [**35** 62]. Variety of conducting polymer nanocomposites have been prepared using polyaniline (PANI) [**36** 63], polypyrrole (PPy) [**37** 64], polyphenylene vinylene (PPV) [**38** 65], poly (3,4-ethylenedioxythiophene) (PEDOT) [**39** 66] as hosts for inorganic metal, metal oxide and ceramic nanoparticles as guest materials.

Core-shell conducting polymer nanocomposites

Among the inorganic-organic nanocomposites, the *core-shell* structures have attracted much more scientific interest and have become more popular leading to some interesting nanocomposite synthesis. In this technique, different metal and metal oxide nanoparticles are encapsulated in the core of conducting polymers.

Table 4. Selected conducting polymer/clay nanocomposites

Polymer	Layered clay	Synthesis method	Structure of nanocomposite	Reference No.
olyaniline	MMT CdS	Emulsion	intercalation	**43** 70
		Micro-emulsion	intercalation	**44** 71
		in situ	intercalation	**34** 61
		ex situ	Not mention	**34** 61
		Chemical-oxidation	Not mention	**34** 61
	Om-MMT	Dispersion	Exfoliation/intercalation	**24** 51
	Maghnite-H+	*in situ*	intercalation	**45** 72
	Cloisite 15A	*in situ*	Not mention	**46** 73
Polypyrrole	MMT	Chemical-oxidation		**47** 74
	Bentonite	Chemical-oxidation	intercalation	**48** 75
	Hydroxy appatite	Electropoly-merization	Not mention	**49** 76
	VMT	Chemical-oxidation	intercalation	**50** 77
Polythiophene	Modified MMT	*in situ*	intercalation	**37** 64

Core-shell structured silica (SiO$_2$) nanoparticles based PANI and Ppy nanocomposites were synthesized in stable colloidal forms, where SiO$_2$ was used as the core [**40** 67]. Colloidal PPy-Au *core-shell* structured nanocomposites have been synthesized by a template-guided polymerization technique [**41** 68]. Deng and co-workers have reported the synthesis of *core-shell* structured ferromagnetic (Fe$_3$O$_4$)-cross linked

PANI nanocomposites. This composite shows *core-shell* morphology in aqueous solution [**42** 69]. Layered clays, synthesis method, structure of nanocomposites of selected conducting polymer/clay based nanocomposites are presented in **Table 4.**

Hematite/silica/polypyrrole (Fe_2O_3/SiO_2/PPy) ellipsoidal sandwich composite spheres as well as SiO_2/PPy ellipsoidal hollow capsules with movable hematite as cores and Ppy as shell were successfully fabricated by *core-shell* technique [**40** 67]. Polypyrrole-coated silver nanocomposite have been synthesized by one step aqueous chemical oxidation dispersion polymerization technique from pyrrole monomer using silver nitrate as an oxidant [**51** 78]. Electromagnetic functionalized *core-shell* nanocomposites of polypyrrole (PPy) were prepared by a self-assembly process [**51** 78]. Yang *et al.* have reported that they prepared novel sunflower-like organic-inorganic composites using smaller conductive polypyrrole and spherical silica particles through an *in situ* route by self-assembly polymerization process. For this preparation chitosan was employed as a modifying agent on silica surface [**52** 79]. Polypyrrole (PPy)-coated Ag composites were synthesized by interfacial polymerization process in the presence of polyvinyl pyrrolidone (PVP) by Feng *et al.* [**51** 78]. *Core-shell* nanocomposites of CuO/PANI [**53** 80], Fe_2O_3/PANI [**53** 80], In_2O_3/PANI [**53** 80] and Fe_2O_3/SiO_2/PANI [**53** 80] were successfully prepared using a double-surfactant-layer assisted polymerization method. Chuang and Yang [**54** 81] have reported the preparation of CeO_2/PANI (CeO_2/PANI) *core–shell* nanocomposites via chemical oxidation method using aniline as monomer and CeO_2 as an oxidant as well as nanomaterials. Synthesis of metallic copper nanoparticle coated with polypyrrole was very recently reported by Kobayashi *et al.* [**55** 82].

Solution casting

In this technique, homogenous dispersion of organoclay (Na^+ MMT) was added to solution of ammonium salt of hexadecylamine. The solution was spread onto a glass plate and the solvent was evaporated by taking appropriate time for drying to form nanocomposite [**56** 83].

Solubility of polyaniline

Solubility

The acid doped form of PANI is insoluble in aqueous solutions as well as in most common organic solvents, but soluble in concentrated sulphuric acid [**57** 84]. When the emeraldine salt of PANI is deprotonated to form the insulating emeraldine base of PANI, it can be solubilized in a number of organic solvents [**58** 85], such as N-methyl pyrrolidone (NMP), dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), m-cresol, chloroform ($CHCl_3$) and tetrahydrofuran (THF). The process of dedoping effectively removes the cationic charges upon the conducting polymer backbone and that reduces the ionic character, which is more amenable to dissolution. Gelation of the conducting polymer commonly occurs at high concentrations of the

EB solutions. This result helps to increases viscosity due to formation of strong interchain hydrogen bonding between the amine hydrogens and nearest neighbour imine nitrogens. A novel route to solubilize the ES form is by the use of functionalized protonic acid dopants such as sulphonic acids (camphor sulphonic acid, dodecyl benzene sulphonic acid) [**59** 86].

Substituted Polyaniline

Solubility of PANI can be improved by polymerizing a derivative of aniline, particularly by choosing the substituent which has solubilising effect. There are two types of substituents. One substituent occurs at N-atom and other is on the ortho-and meta-position of benzene ring. The different substituents are alkyl [**60** 87], alkoxy [**61** 88] groups, phosphoric and sulphonic acid [**62** 89] groups. The acid group substituted PANI was found to be more soluble, some of them being water soluble and also showing higher thermal stability. Polymerization of substituted anilines can also be carried out either chemically [**60** 87] or electrochemically [**60** 87]. The major drawback of these rings substituted PANIs is the fact that solubility is achieved at the cost of conductivity [**60** 87].

Functionalized protonic acid as dopant

Cao, Smith, and Heeger [**63** 90] synthesised metallic form of PANI using functionalized protonic acids and simultaneously resulted PANI complex soluble in common organic solvents. The functionalized counter ion acts as 'surfactant' and the charged head group is ironically bound to the oppositely charged protonated PANI chain, and the 'tail' is chosen to be compatible with non-polar or weakly polar organic liquids [**63** 90]. This is called 'counter-ion' induced processability.

Blends of polyaniline

Conducting blend is another kind of conducting materials, which supports to improve the solubility and that, is found from literatures [**64-66** 91-93]. It is a physical mixture of two or more polymers with different chemical compositions. Improvement of the PANI processability resulted in the fabrication of several types of conductive blends of PANI [**64-66** 91-93]. The main purpose of making blends is to introduce flexibility and toughness to PANI thereby making it melt processable. A phase separation between the two components of the blends leads to decrease of mechanical strength of the material [**67** 94]. However, by keeping the PANI composition less than 16 wt%, materials with good flexibility blend can be obtained. Several conductive blends of PANI salt with thermoplastic polymers such as polystyrene [**65** 92], polyamides [**68** 95], poly (vinyl alcohol) [**69** 96], poly (vinyl chloride) [**70** 97], and so forth have been extensively studied.

Copolymers

Copolymer is another class of materials with improved solubility. It is generally carried out to combine the diverse physicochemical properties of different polymers to form a single polymeric system. Copolymerization of aniline with ring or N-substituted anilines leads to polymers which have conductivity like PANI and solubility of substituted anilines [**61, 62** 89,88].

Polyaniline dispersions

Dispersion polymerization is a well-known technique for the synthesis of conventional polymer in both aqueous and non-aqueous media [**6, 71, 72** 18,98,99]. Colloidal dispersion is one of the widely used and technologically important ways for tackling the problem of poor solubility of PANI [**73, 74** 100,101]. Dispersion of PANI is used in the preparation of blend with thermoplastic polymers.

Polymer stabilized polyaniline dispersions

Various polymeric steric stabilizers such as ethyl cellulose [**75** 102], carboxymethyl cellulose [**76** 103], poly (vinyl alcohol) [**69** 96], poly (vinyl methyl ether) [**77** 104], poly (N-vinylpyrrolidone) [**78** 105], etc. are employed for the synthesis of PANI in colloidal form or as suspension by chemical polymerization using aniline precursors. According to Armes and co-workers [**73** 100], they have synthesized colloidal PANI by chemical grafting of PANI onto several tailor made copolymer surfactants. The resulting polymer (PANI) is insoluble in solvents and its macroscopic coagulation is prevented by steric stabilizers [**75** 102]. The possible synthetic routes and the properties of PANI colloids have been reviewed by Stejskal [**75** 102]. The morphology and the size of colloidal particles are strongly depended on the steric stabilizer, oxidizing agent and reaction conditions [**79** 106]. On the other hand, the use of polymeric stabilizers in PANI drastically lowers the electrical conductivity of PANI [**80** 107].

Processability

Processability is one of the major issues in the synthesis of conducting polymers for commercial applications in different areas. These applications of conducting polymers like PANIs are limited due to the lacking of solubility and processability. A number of approaches have been investigated to improve the processability of PANI.

Generally, alkyl and alkoxy substituted aniline monomer is polymerized to improve the solubility of the polymer in organic solvents. But, it has a negative influence on the conductivity [**60, 61** 87,88]. The first known examples of water soluble conducting polymers reported in 1987 are the sodium salts of poly -3-(2-ethane sulfonate) thiophene and poly -3-(4-butane sulfonate) thiophene [**81** 108]. These

polymers are self-doped Polythiophenes. The electrochemical polymerization of aniline carboxylic acid isomers has been recently reported [**82** 109]. Poly (o-amino benzyl phosphoric acid) is another type of self doped conducting polyaniline synthesised and the polymer was soluble in dilute ammonia solution but insoluble in water [**83** 110]. Electro-co-polymerization of aniline and o-aminobenzenesulphonic acid formed sulfonated PANI which was soluble in neutral pH [**84** 111].

Introduction of sulphonic acid group to the PANI chain makes soluble PANI which is self-doped and is known as Sulphonated PANI (SPAN). By chemical and electrochemical method, methoxyaniline sulphonic acid is polymerized [**85-87** 112-114]. Another type of conducting PANI was synthesised for improving the processability as well as redox-activity over a wide pH range [**88-90** 115-117]. However, these conducting polymers have low electrical conductivity.

In a solution processing route, nanostructured materials were prepared from colloidal dispersions with reasonable conductivity using a range of steric stabilizers. These used different surfactant micelles such as dodecyl benzene sulfonic acid [**91** 118], naphthalene sulphonic acid [**92** 119], polyethylene oxide (PEO) [**93** 120], water soluble polymers such as poly (N-vinyl pyrrolidone) [**94** 121], organic dopants [**95** 122] and silica colloids [**96** 123].

Polyaniline can also be formed using aniline as monomer and polyelectrolytes such as polystyrenesulphonic acid [**97** 124], polyacrylic acid [**98** 125] and poly (2-acryloamido-2-methyl-1-propane sulphonic acid) [**99** 126] as template. The role of the polyelectrolyte template is to align aniline monomer and promote head-to-tail coupling. The polyacid template was thought to provide a low pH for growth of water soluble PANI and also the necessary counter ions for doping PANI to the conducting form [**97** 124]. The polymerization reaction rate was faster compared to ordinary chemical polymerization owing to the high local concentration of aniline and hydrogen ions on the template matrix (polyamide) [**99** 126]. The use of these non-conducting polyelectrolytes resulted in low electrical conductivity of the water dispersible PANI [**100-102** 127-129].

Recently, PANI nanofibers were synthesised by using interfacial polymerization at aqueous/organic interface or rapid mixing of monomer and oxidant aqueous solutions in controlled ratio [**103** 130]. These methods have the advantage of stabilizer-template free polymerization and ease of purification. The nanofibers have diameters between 30 and 50 nm and make relatively stable dispersion at pH around 2-3 [**104** 131].

Polyaniline composites

The preparation of conducting polymer composite blends with common polymers in order to improve the mechanical properties and processability of ICPs has been investigated [**105** 132]. In general, there are two main methods used to produce composites: synthetic method based on polymerization of aniline in a matrix polymer and blending methods via mixing a previously synthesised polyaniline with a matrix

polymer.

Characterization techniques

Generally, the prepared materials are needed three types of characterizations such as spectroscopic analysis, structural analysis, and electrical analysis (DC electrical conductivity, temperature dependent DC conductivity with and without field, and gas sensor measurements).

Spectroscopic characterization for chemical structure

The different non-destructive techniques (NDT) such as NMR (H^1NMR), ESI-MS, FTIR/ATR-FTIR, and UV-Visible are generally required to characterize the prepared materials.

Proton nuclear magnetic resonance (H^1NMR)

H^1NMR technique is one of the NDT. Molecular structure was investigated using Nuclear Magnetic Resonance (NMR) spectrometer (Bruker DRX-500MHz spectrometer). The molecular structure of synthesised salt (AA and Ani) and its polymer was also characterised by NMR technique. In NMR spectrometer, radiofrequency (RF) is used as NMR source and to induce transition between different nuclear spin states of samples in a magnetic field. By the application of strong magnetic field to the samples, their spins are reoriented, *i.e.*, aligned with the field or against the field [**106** 7].

Furthermore, splitting of the spectra lines arises due to interactions between different nuclei, which provide information about the proximity of different atoms in a molecule. We explored the H^1NMR to investigate the molecular structure. Orientation parallel to alignment of applied force is lower in energy. When nuclei are irradiated with RF radiation the lower energy nuclei flip to high state and nuclei is said to be in resonance, hence the term NMR.

For this technique, particular deuterated solvent is required and it is called lock solvent. In my thesis work, deuterated chloroform ($CDCl_3$)/deuterated dimethyl sulphoxide (d_6-DMSO) was used. Prepared samples were dissolved in a $CDCl_3$/d_6-DMSO to form deuterated solution. The prepared NMR samples are run in 5 mm glass NMR tubes. An NMR tube was filled prepared sample and then, the sample tube was exposed to RF radiation in the spectrometer and data were collected. The chemical shifts of the groups are recorded in the range 10-200 ppm with a delay of 2.5 sec. This technique was done to help the analysing the molecular structure.

Mass analysis (ESI-MS)

Mass spectrometry [MS] is an analytical technique which is NDT that

identifies the chemical composition as adduct of a prepared sample on the basis of the mass-to-charge ratio (m/z), called charged ions. Such ionization of mass occurred by electrospray ionization of mass (ESI-MS) technique. The technique is used in both qualitative and quantitative analysis.

Now a days, this technique is more acceptable to identify the large molecules. It fragments the samples [**107** 8] to form charged ions from relatively non-volatile, thermally labile compounds. ESI-MS had as its first uses, the ionization of intact chemical species but now has found wide acceptance in the identification of large molecules. This instrument has ability to form charged ions from relatively non-volatile, thermally labile compounds. Multiple charged ions are generated which serve to extend the useful mass range of the instrument. A mass spectrometer generates multiple ions from the sample under investigation; it then separates them according to their m/z, and then records the relative abundance of each ion type.

The first step in the ESI-MS spectroscopic analysis of compounds is the production of gas phase ions, basically by electron ionization. This molecular ion undergoes fragmentation. Each primary product ion derived from the molecular ion, in turn, undergoes fragmentation, and so on. The ions are separated in the mass spectrometer according to their m/z ratio and are detected in proportion to their abundance. A mass spectrum of the molecule is produced. It displays the results in the form of a plot of ion abundance verses m/z ratio. Ions provide information concerning the nature and the structure of their precursor molecule. In the spectrum of a pure compound, the molecular ion if present, appears at the highest value of m/z (followed by ions containing heavier isotopes) and gives the molecular mass of the compound. In the thesis work, mass spectra were obtained from AXIMA-CFR laser desorption ionization flying time spectrometer (COMPACT). In this work, we used gel-like (prepared salt) samples. It helped to evaporate solvent easily. Typical solvents for electrospray ionization were prepared by mixing water with volatile organic compounds like methanol and acetonitrile. Acetic acid was added to prepared typical solvent. That was done because to decrease the initial droplet size and increase the conductivity of prepared materials like salt.

Fourier transformation infra-red (FTIR) spectroscopy

Like NMR and ESI-MS, FTIR/ATR-FTIR is a NDT technique. This technique is used to analyse the presence of functional groups, formation of chemical linkage between used materials and interaction between nanomaterials and polymers, metal oxygen bond and removal of organic and other phases with have been investigated using a FTIR/ATR-FTIR spectrometer (Nexus-870, Thermo Nicolet Corp, and USA). The instrument parameters were kept constant (50 scan at 4 cm^{-1} resolution, transmittance/absorbance mode). In this spectrometer [**108, 109** 9,10], the IR radiations from an IR source are passed through the sample and the amount of energy adsorbed/transmitted was recorded by suitable detector and is guided through an interferometer where a Fourier Transform is performed on the output signal.

For this technique, powder, liquid and solid film samples were used. Solid film samples were analyzed in ATR mode. For this measurement, the powdered samples were prepared by making pellet. At first, dry KBr are grinded using mortar pestle followed by addition of small amount of prepared samples. Further, sample mixture is grinded. Then it put in die and placed inside (appropriate place) the hydraulic pressure and compacted the samples by pressure (5 kg.f).

The pellet (13 mm diameter, 0.3 mm thick) so prepared was used for IR characterization. Liquid samples was directly put on KBr pellet/quartz glass plate and used for this characterization. Before running the samples, a background spectrum was collected. Then pellets samples were put in a sample holder. The pellets are exposed to IR radiation in the spectrometer and data were collected. This technique was done to characterize the bonding type of the molecules and for each type of bonding it produced characteristic absorption bands.

Ultraviolet-visible (UV-Vis) spectroscopy

UV-Vis spectroscopy is also one type of NDT technique. The UV−Vis spectra of the prepared materials were recorded by using a Micropack UV−VIS−NIR, DH 2000. The wave length of spectrum was taken from 200 to 800 nm. Powdered, liquid, and solid film samples were used for doing UV-Vis characterization. Transparent solvent was used within the wavelength range for making required solution. In this spectroscopy, we choose the wave length in the UV and Visible region and expressed in nanometre. For this analysis, transparent solution is required. UV−Vis light is an electromagnetic radiation and obtained from different sources (tungsten lamp or tungsten-halogen lamp or deuterated lamp). The emitted energy was passed through the molecules containing π-electrons or non-bonding electrons. It absorb/reflect and cause excitation from highest occupied molecular orbital to lowest unoccupied molecular orbital, *i.e.*, HOMO to LUMO. It is detected by the detector and spectrum is obtained in computer. In this thesis work, I have prepared desired transparent solution using small amount of synthesized powder as starting materials and DMSO/NMP as solvent.

Such solution was made by taking 5 mg synthesized materials and 20 mL DMSO/NMP. For recording the spectrum, quartz cell (length = 5 cm) is commonly used. These require approx. 3 mL of solution and were placed in the path of light beam and spectrum was recorded by varying the wavelength of incident light. The sample cell should be rinsed three to five times with DMSO/NMP solvent before filling with the pure solvent that will be used in the measurement. Most UV-Vis instruments can analyze solid samples or suspensions with a diffraction apparatus but this is not common. Base line was corrected before recording the spectra. This technique was performed for studying the variety of electronic transitions [**110** 11].

Structural and Morphological Characterizations

X-ray diffraction (XRD) technique

X-ray diffraction (XRD) is a powerful non-destructive technique to determine crystalline/amorphous structure [**111** 12], intercalated/exfoliated/delaminated nanostructure [**111** 12] of clay based composites. It is also estimates various structural parameters such as crystallite size (D), inter layered-spacing (d), etc. X-rays are generated from Cu target with a characteristic wavelength (λ) which can be obtained from the expression [**112, 113** 13,14] as shown in equation (1)

$$E = h\upsilon = h\frac{c}{\lambda}...................(1)$$

Where, h is the Planck's constant (6.62×10^{-34} joule), c is the velocity of light (3×10^{-8} m/s) and E is the energy of the radiation. The wavelength of X-ray is comparable to the size of atoms.

The basic principle of X-ray diffraction is based on constructive interference of X-rays (monochromatic) and prepared samples. The interaction of the incident X-rays with the samples produces constructive interference and the diffracted rays are generated which is satisfies the Bragg's law ($n\lambda=2d\sin\theta$). By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered materials. Conversion of the diffraction peaks to d-spacing allows the identification of the materials because each material has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacing with standard reference patterns.

In the present thesis work, most of the X-ray diffraction patterns were recorded using CuKα radiation (wavelength, λ=0.154 nm). During the operation, XRD was operated at 40 kV and 20 mA. The powder samples were placed on a quartz sample holder at room temperature and were scanned at diffraction angle 2θ from 5° to 45°. The sample is kept in a Perspex holder.

Electron Microscopies (SEM/FESEM or TEM/HRTEM)

Scanning Electron Microscopy or Field Emission Scanning Electron Microscopy

Surface morphologies of prepared materials were analyzed by electron microscopies such as SEM/FESEM or TEM/HRTEM. SEM/FESEM is a microscope that uses electrons in place of light to produce image [**114** 15]. It is a surface phenomenon. In this measurement, the electron beam produced from electron gun is focused on a small portion of the sample that is kept in vacuum. Detector collects the output signals during the interaction of electrons with the sample and that is sent to a computer. This forms the final image. Two types of electron gun are used. One is

thermionic and the other one is field emission.

The electrons emitted from the electron gun are accelerated by applying a high electric potential. The scanning of the electron beam over the sample surface is controlled by deflecting the electron beam using a scanning coil. In vacuum condition, both FESEM/SEM are used to produce image. Therefore, special preparation technique is needed for the sample to avoid moisture absorption. All nonconducting materials need thin layer of conducting coating. This is done by 'sputter coater'. Operating voltage was 4 kV. Such coater uses an electric field and argon gas. The sample is placed in a small vacuum chamber. The argon gas is ionized in the applied electric field to form argon ion (Ar^+). The argon ions knock gold atoms from the surface of the gold foil and get deposited on sample.

High Resolution Transmission Electron Microscopy (HRTEM)

It is also a special kind of electron microscopic tool that uses highly accelerated beam of electron as illumination for microscopic analysis. Such beams are passed through the electron transparent samples. The interaction occurred between electron and atoms of the sample. The transmitted electrons are then focused by the objective lens into an image. In HRTEM, electromagnetic lenses are used to guide the electron beam through the microscope. The specimen preparation for HRTEM experiment should be important for getting good results. The main criteria of sampling are artifacts free. The detailed sampling procedure was found in the journal [**115** 16]. In this investigation, pellet samples were used for doing HRTEM.

Thermal Characterization
Thermogravimetric (TG) Analysis

TGA analysis is a type of thermal analysis that measures mass change of materials [**116** 17] with change of temperature. The purpose of doing such experiment is to measure volatile content, thermal stability, degradation characteristics, etc.

Differential Scanning Calorimetric (DSC) Analysis

Differential scanning calorimetry (DSC) is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. The technique provides qualitative and quantitative information about physical and chemical changes that involve endothermic or exothermic processes or changes in heat capacity using minimal amounts of sample. It has many advantages including fast analysis time, typically thirty minutes, easy sample preparation, applicability to both liquids and solids, a wide range of temperature applicability and excellent quantitative capability [**117** 18].

There are two types of DSC systems in common use. In power compensation

DSC, the temperatures of the sample and reference are controlled independently using separate, identical furnaces. The temperatures of the sample and reference are made identical by varying the power input to the two furnaces; the energy required to do this is a measure of the enthalpy or heat capacity changes in the sample relative to the reference.

DSC has been used in the evaluation of small transitions such as multiple phase transitions in liquid crystals and those due to side chains in polymers which cannot be resolved by most other techniques. It allows accurate determination of temperatures associated with thermal events. Temperature can be calibrated with respect to one or more standards which allow highly accurate, precise and reproducible values. The technique reveals the thermal history imparted to thermoplastics as a result of different processing conditions. The information generated can be used to vary heating rates to deliver the required degree of crystallinity.

Differential scanning calorimetry (DSC, Diamond Perkin-Elmer, USA) was used for determination of crystallization. Samples (5-10 mg) were placed in sealed aluminium pans and scanned under a constant nitrogen purge (20 mL/min). Subsequently, the samples were heated from 30 °C to 200 °C at a rate of 20 °C/min, held at 200 °C for 2 min, cooled to 30 °C at the same rate and held for 2 min to stabilize. Finally a second scan was carried out from room temp to 200°C. The results crystallization temperature (T_c), melting temperature (T_m) and glass transition temperature (T_g) were noted from the second scan.

In the current research work, DSC has been carried out for the PANI-ES/Cloisite 20A nanocomposites and acrylic acid based PANI to investigate the crystallization behavior of the samples. Sample preparation work can greatly affect the results. So, specimen preparation should be as gentle as possible. The vertical specimen has smaller contact area and so it takes longer time to melt. Large contact area promotes heat transfer. Polymers can absorb water, *e.g.,* polyamides and this affects their properties as well as results. For DSC study, specimen mass should be 5-20 mg.

Electrical Characterizations

DC conductivity measurement at Room temperature as well as temperature dependent (presence and absence of magnetic field)

DC conductivity measurement at room temperature as well as temperature dependent (presence and absence of magnetic field) is an important electrical characterization to show the electrical nature of materials at different conditions. For DC conductivity measurement a four probe set-up was used as shown in **Fig. 3.**

Usually, resistivity of semiconductor is measured by four probes technique. It is a one of the standard electrical measurement method. In this investigation, I have used linear four probe technique to measure both room and low temperature resistivity. Pellet and solid film samples were taken for this measurement. Four electrical contacts

were made by attaching copper wires onto the sample surface through silver paste. In this technique, four probes contact points were arranged linearly in a straight line at equal distance (S) from each other. For room temperature measurement, the sample was fixed on insulating plate where four probes are connected.
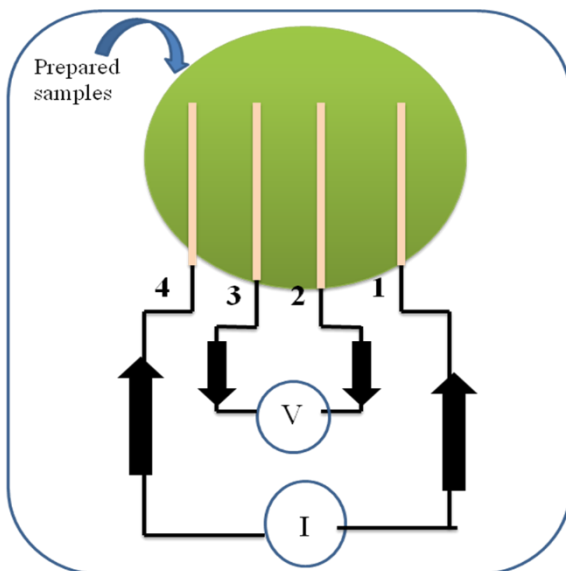

Figure 3. Schematic representation of linear four probe set-up

The output voltage is related proportionally to the applied current. Such type of contacts was called ohmic. According to four point probe method, the resistivity (ρ) was calculated using the relation [**118** 19]

$$\rho = 2\pi S \left(\frac{V}{I} \right) \dots\dots\dots\dots\dots(2)$$

Where S is the probe spacing in centimetre (*cm*), which was kept constant, I is the supplied current in millampere (*mA*) or nanoampere (*nA*) and the corresponding voltage was measured in volt (*V*) or millivolt (*mV*). The conductivity (σ) was calculated using the relation [**118** 19]

$$\sigma = \frac{1}{\rho} \dots\dots\dots\dots\dots(3)$$

For low temperature resistivity measurement, sample was placed in a specific chamber and the pressure was maintained at 10^{-5} torrs. The Lakeshore (model 331) temperature controller was connected. Then, we measured DC resistivity. A constant current is passed through the two side probes and measured voltage in the two middle probes. A DC current source (Keithley 220 programmable) was taken. Different

millampere/nanoampere current was applied and corresponding voltage was measured. Voltage across the terminals was measured using Keithley nanovoltmeter (model 2182). For In addition, the resistivity measurement with a particular magnetic field is a function of temperature which is important for calculating localization length (L_{loc}). Determination of other different transport parameters [119 20] such as Density of states at Fermi level ($N(E_F)$), Motts characteristics temperature in Kelvin (T_{Mott}), Mott's hoping distance ($R_{Hop, Mott}$ in nm at 300 K) and the energy difference ($\Delta_{Hop, Mott}$) between the sites in the Mott's limits is calculated using L_{loc}. These are the important parameters to understand the conduction mechanism.

Magnetoresistance (MR) was investigated using a Helium Compressor (HC) (model HC-4E1)–sumitomo cryostat (model Ganis research CO, INC) equipped with 0.8T superconducting magnet (Lake shore electromagnet). For the controlling and measurement of the temperature, we used Lake Shore 331 temperature controller. Magnetoresistance (MR) measurements were performed up to 4000 Gauss (for acid doped membrane based PANI-ES composites) and 5000 Gauss (for Cloisite 20A based composites) and different temperatures 100 K, 200 K, 250 K, 300 K using a computer-controller measuring system.

Gas sensing measurement

For gas sensing studies, the prepared composite film (~25 °C) was used. Schematically, gas sensing measuring set up is shown in **Fig. 4.** The set up mainly consists of three sub units and are gas deliver unit, reactor unit and measurement unit.
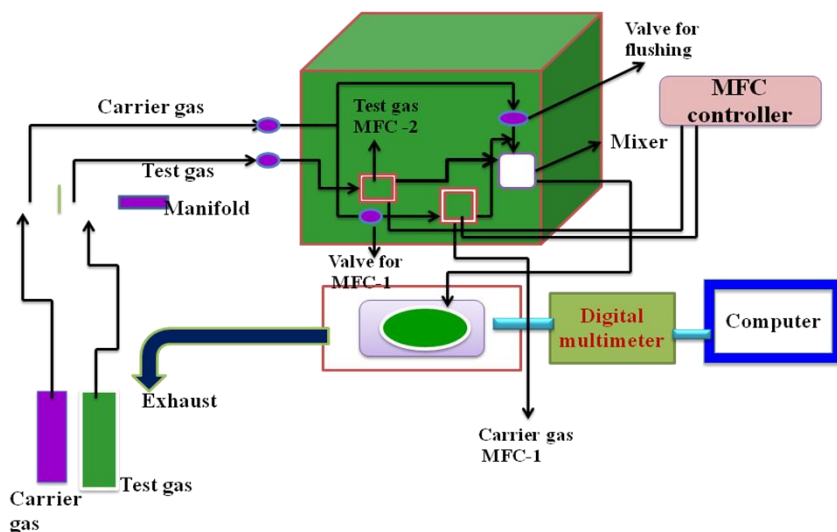
$$\text{Re sponse}\,(\%) = \frac{R_a - R_g}{R_a} \times 100 ....(4)$$

Figure 4. Schematic dynamic gas sensor set- up unit

For the sensing measurements, the surface of the sensing material is electroded with silver paste strip of 8 mm length, 1.5 mm width, and separated from each other by 4 mm. The methane gas sensing behaviour was estimated by measuring the resistance change before and after gas exposure. This measurement was done using an electrometer (6517A, Keithley instruments, USA) in a specially designed sensing-setup [**120** 21] under dynamic flow of methane gas. The pre−diluted (~10,000 ppm) reducing gases (methane) in nitrogen are mixed with carrier gas (air) using a mixing unit before flowing into the reactor unit. The mass flow controller and electrometer are all interfaced with a PC equipped with a GPIB card (National Instruments) and Labview 8.5 (National Instruments) software.

To evaluate the gas sensing characteristics of the polymer membrane, its planar resistance transient were measured as a function of temperature and gas concentration. From the measured value of equilibrium resistance in air $\left(R_a\right)$ and gas $\left(R_g\right)$ the response of the sensor surface towards reducing gases was calculated using the relation [**120** 21].

5. Conclusions

PMMA/PANI composite films are prepared by *insitu* polymerization technique. HCl, H_2SO_4, and H_3PO_4 are used dopants, separately, during the polymerization reaction. Different desired chemical groups of PMMA film, PANI and PMMA/PANI composites are confirmed from ATR-FTIR spectroscopy. Polaron band is shown in UV-Visible data and are confirmed the formation of emeraldine salt (ES). A drastic increment of band gap of the doped samples is found. I-V characteristics without magnetic field of doped PMMA/PANI composites are revealed ohmic behaviour at room temperature. Highest DC conductivity without magnetic field is found to be 0.1421×10^{-2} S/cm for H_2SO_4 doped PMMA/PANI composite. Decreased DC conductivity data with increased magnetic field is observed. Temperature dependent DC conductivity data of HCl doped composite is indicated the semiconducting behaviour.

2.4. Acknowledgments

2.5. References

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