

# Chapter 1

## Fundamentals on Polyaniline based Composites

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### Abstract

The background of work carried out highlighting on polyaniline, N-substituted polyaniline and acid-doped polyaniline. The problems associated with this polymer and promises it hold are also discussed. It also provides introduction to the nanocomposites of polyaniline/nanoclays, and polyaniline/polyacrylic acid. As well, we have described the polymer stabilized intrinsically conducting polymer composites. The state of the art polymer stabilised intrinsically conducting composites have been reviewed. At last, we have reviewed on the CH<sub>4</sub> gas sensing since it has been recognized as one of the inflammable gas sensors. The main problem on the CH<sub>4</sub> gas sensor lies on its room temperature operation and detection of low ppm level concentration.

### Keywords

Polyaniline, Nanocomposites, N-substituted polymer, Doping, Conductivity, Variable range hopping (VRH), Magnetoresistance, Gas sensor

### Introduction

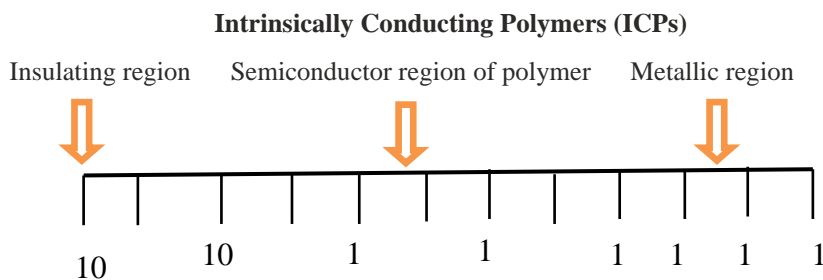
In recent times, polymers are widely used multipurpose materials in different fields due to the some advantageous nature. These are flexibility, tailorability, processability, environmental stability, low cost, light weight, etc. [1]. Polymers are used as electrically insulating materials in various electronic devices such as covering insulating materials on electrical wire, switches, insulating coating on electronic circuit board, etc. [1]. The band gap of these polymers are reported more than 10 eV and also, the surface resistivity is higher than 10<sup>12</sup> ohm.cm [1].

The work on the discovery of conducting polymers began in the year of 1975. First, polyacetylene was discovered by Shirakawa [2] as conducting polymer, which

is called a linear conjugated organic polymer. On the other hand, the material showed metallic conductivity after the doping by iodine, which was reported after the discovery of polyacetylene (PA) [2]. This gave rise to a surge of activity directed towards the exploration of synthesis and characterization of this class of materials, also known as ‘Synthetic Metals’ [3]. The desirable properties of the conducting polymeric materials can be achieved among other processability at the molecular level by modifying the parent monomers.

## 1. Conducting Polymer

In the conducting polymeric system, it contains a highly delocalized  $\pi$ -electronic structure with alternate single and double bonds. The alternation of bonds generates energy difference between highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) and it can be readily oxidized or reduced [4]. Intrinsically conducting polymers (ICPs) are also known as ‘synthetic metal’ or simply called ‘synmet’ because of their metallic or near metallic conductivity. The scientific community has shown much interest in this field after the award of Nobel Prize (2000) for the discovery and development of ICPs. ICPs contain alternatively single bond and double bond in the backbone. The  $\pi$ -electrons are loosely bound and it can delocalise throughout the polymer chain [5]. In neutral state, the ICPs become insulator and they become conducting only after incorporation of electron acceptor or electron donator through a process known as ‘doping’. Most of the ICPs show conductivity in semiconducting region (Fig. 1).

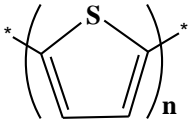
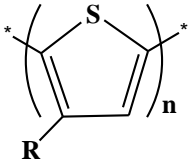
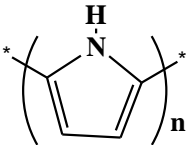
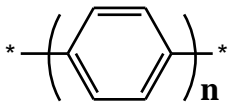
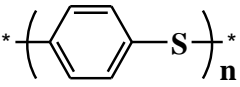
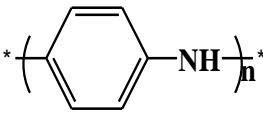


**Figure 1.** Conductivity of electronic polymeric materials [3]

In the ICP family, PA is the first member and exhibit high conductivity. Although, PA is not environmentally stable but it has led to the discovery of other conducting polymers such as polypyrrole, polythiophene, polyphenylene, polyphenylene vinylene, polyaniline, etc. The molecular structure, doping materials and conductivity (S/cm) of a few ICPs are shown in **Table 1**.

The electrical behavior of these polymers and their derivatives is similar to that of polyacetylene. Moreover, they show higher stability and better processability [3,6]. Of all these conducting polymers, polyaniline (PANI) is now establishing itself as a novel material due to its potential technological applications and low cost of synthesis [7].

**Table 1.** List of some ICPs with doping materials and conductivity value (S/cm) [5]

Polymer type	Structure	Doping materials	$\sigma$ (S/cm)
Polyacetylene	$*-(CH)-_n^*$	I <sub>2</sub> , Br <sub>2</sub> , Li, Na, AsF <sub>5</sub>	10000
Polythiophene		BF <sub>4</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>	1000
Poly(3-alkylthiophene)		BF <sub>4</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>	10000-1000
Polypyrrole		BF <sub>4</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>	7500-500
Polyphenylene		Li, Na, AsF <sub>5</sub>	1000
Polyphenylene Sulfide		AsF <sub>5</sub>	500
Polyaniline		HCl	200

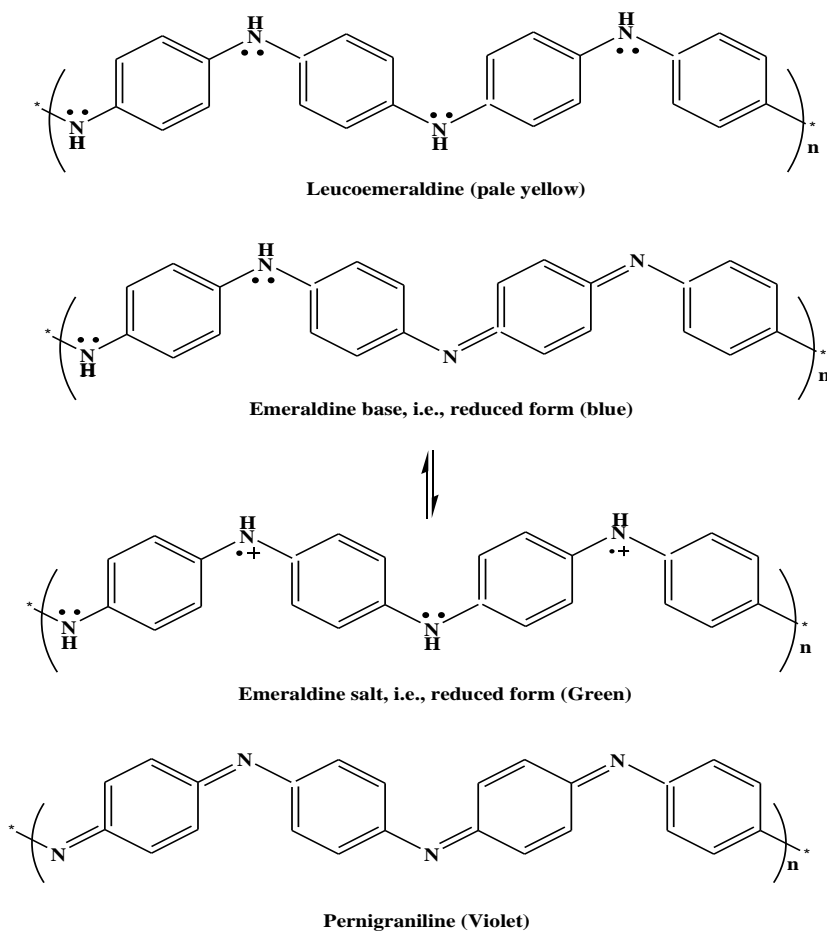
## 2. Polyaniline (Pani)

PANI has been investigated extensively for few decades. It has attracted special attention towards scientific community/technologist as a conducting material for several important reasons. These are inexpensive; polymerization reaction is straightforward and proceeds with high yield and excellent stability. In early discovery, this product was known as ‘aniline black’ [8]. An attention has been focused on processing, *i.e.*, synthesized easily both by electrochemical and chemical

oxidation processes and sensitivity towards environment due to the proton activity [9].

## 2.1 Structure of Polyaniline

Green and Woodhead [10,11] have shown PANI as a chain structure which is obtained from aniline molecules and coupled head-to-tail manner at the para position of the phenyl ring. The diversity in physicochemical properties of PANI is attributed to the  $-NH-$  group. These properties come from the combination of amine and imine segments present in PANI chains. Amine and imine segments generate several oxidation states and produce different forms of PANI materials. These are fully reduced leucoemeraldine, fully oxidized pernigraniline states, and also other form, which is shown in **Scheme 1**. The different forms of PANI can be readily converted to one another by simple redox methods (Scheme 1.1). Out of several possible oxidation states, the 50 % oxidized emeraldine salt state shows electrical conductivity [12].



**Scheme 1.** Various possible oxidation states of PANI [12]

## **2.2. Synthesis Of Polyaniline**

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. [9, 13-32].

## **3. Mechanism of Conductivity**

The electrical conductivity of doped conducting polymers can be varied up to more than ten orders of magnitude. Charge transport in these polymers has been extensively investigated [29]. All conducting polymers have intrinsic defects which are introduced during polymerization. Removal of a charge from the valance band generates a radical cation whose energy lies in the band gap. Such radical cation which is partially delocalised over some polymer segments is called a 'polaron' Formation of polaron is associated with the distortion of lattice and the presence of two localized electronic states in the gap. According to the model proposed by Brazovski-Kirova [33], formation of a polaron leads to the possibility of three new optical transitions. A bipolaron is also associated with structural deformation and the two charges are not independent but act as a pair. Application of an external electric field makes both polaron and bipolaron mobile via the rearrangement of conjugation.

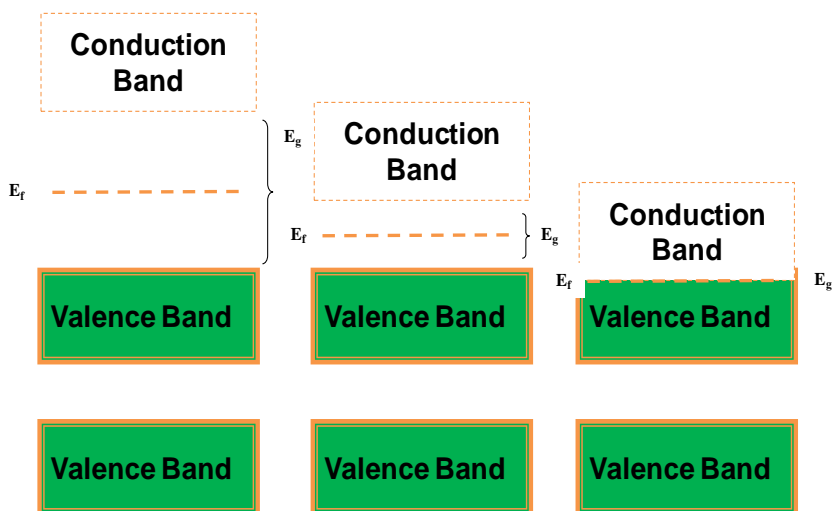
In the case of PANI polymer, the charged species are formed during protonation of the polymer, which are subsequently responsible for the increase in conductivity [20]. Several other mechanisms are also proposed for the conductivity of PANI polymer. Salaneck and co-workers [34,35] studied a one-dimensional variable range hopping or three-dimensional fluctuation-induced tunnelling models.

### **3.1. Metal-Insulator (M-I) Transition In Doped Conducting Polymer**

Heavily doped conducting polymers show many electrical properties. These are electrical conductivity, Pauli temperature independent magnetic susceptibility, etc. The doping of conducting polymers produces in inhomogeneity or phase-segregated regions. Therefore, the conducting polymer contains both crystalline and amorphous regions. The amorphous region affects the transport. As a result, the metallic features in the bulk transport are severely limited due to strong disorder [36]. The disorder can result in localization of states. If the magnitude of the disordered potential is large compared with the bandwidth, all states become localized, and the system will be an insulator. In such a state, there is no gap in the density of states. In insulating state, Fermi level ( $E_f$ ) lies in an energy interval in which all density of states are localized and is known as Fermi glass. In a Fermi glass, the conductivity is activated. The energy band gap of materials is shown in **Scheme 2**. At high temperatures, the activation energy is a measure of the energy difference between  $E_f$  (which lies in the region of localized states) and the mobility edge, whereas, at lower temperatures, variable-range-hopping transport results from the existence of unoccupied localized electronic states near  $E_f$ . The M-I transition occurs when the disorder is sufficiently weak that

the mobility edges move away from the center of the band toward the band tails such that  $E_f$  lies in a region of extended states.

In M-I transition, the mean free path becomes less than the inter-atomic spacing. This is due to increase in disorder in a metallic system and the coherent metallic transport is not possible [36]. When the disorder is sufficiently weak, the metal shows a transition from the metallic state to insulating state. This transition is known as the Anderson transition, *i.e.*, all the states in a conductor become localized and it converts into a "Fermi glass" [37] with a continuous density of localized states occupied according to Fermi statistics. Although there is no energy gap in a Fermi glass but due to the spatially localized energy states a Fermi glass behaves as an insulator [37]. It has been found that electrical conductivity of a material near the critical regime of Anderson transition obeys power law temperature dependence [36,37].



**Scheme 2.** Energy band gap of materials

Variety of conducting polymers, *viz.*, polyacetylene, polyaniline, polypyrrole, poly (p-phenylene vinylene), etc. have shown M-I transition. It is very interesting observation because the critical behaviour has been observed over a relatively wide temperature range [36-41]. In the metallic region, the zero temperature conductivity ( $\sigma_0$ ) remains finite, and  $\sigma(T)$  remains constant as  $T$  approaches zero [36-44]. In the critical region, the conductivity follows a power law, whereas in the insulator region, transport occurs through VRH among localized states. The disorder is generally recognized in the physics of "metallic" polymers. Till now, the disorder of the metallic polymer and the nature of the M-I transition are not resolved [36-44].

## 4. Application of Polyaniline

Depending on the conductivity and electroactivity character, conducting

polymers are being used various applications. They are described as follows;

## **Group I**

In group applications, conductivity of the polymers is the key parameter. Also, the polymers have some characteristics *i.e.*, lightweight, biological compatibility for ease of manufacturing or cost. Therefore, conducting polymer is employed in electrostatic materials, conducting adhesives, electromagnetic shielding, printed circuit boards, artificial nerves, antistatic clothing, piezoceramics, active electronics (diodes, transistors), aircraft structures. These applications discussed briefly as follows;

**Electrostatic materials:** It is prepared by thin layer coating of conducting polymer on an insulator. it is used to prevent the build-up of static electricity. This is particularly important where such a discharge is undesirable. Such a discharge can be dangerous in an environment with flammable gasses and liquids. It is also dangerous in the explosives industry.

**Conducting adhesives:** it is prepared by insertion of monomer between two conducting surfaces which is allowed to polymerize. The polymerised monomer is promising to stick between them. It is used to stick the conducting objects and is allowed to pass the electric current through them.

**Electromagnetic shielding:** Several electrical devices such as computers, generate electromagnetic radiation, often radio and microwave frequencies can cause malfunctions. This problem can be overcome by inside coating of the plastic casing with a conductive surface. So, the emitted radiation can be absorbed by inside coated with conducting surface.

**Printed circuit boards:** Numerous electrical appliances are used printed circuit boards. In printed circuit board, copper coated epoxy-resins are used. The copper is selectively etched. It is produced conducting lines. These lines are used to connect various devices. The device is placed in holes cut into the resin. In order to get a good connection the holes need to be lined with a conductor. Copper has been used but there is several problems. Therefore, coating method is used. Now, the process is being replaced by the polymerization of monomer. The monomer is formed conducting polymer. Initially the board is etched by potassium permanganate solution. A thin layer of manganese dioxide is formed on the surface of resin. The resin is polymerized by suitable monomer and is produced a layer of conducting polymer.

**Artificial nerves:** Because of biocompatibility nature of some conducting polymers, they may be used to transport small electrical signals through the body. Therefore, it act as an artificial nerves.

**Aircraft structures:** In the present scenario, planes and spacecraft are made up with lightweight composites. The structure makes them weak and is to be damaged from lightning bolts. The damaged part can be saved by coating with a conducting polymer. The electricity can be directed away from the vulnerable internals of the

aircraft.

## Group II

In group II applications, conducting polymer utilizes the electroactive behaviour. Numerous applications such as molecular electronics, electrical displays, sensors (Chemical, biochemical and thermal), rechargeable batteries, solid electrolytes, drug release systems, optical computers, ion exchange membranes, electromechanical actuators, 'smart' structures, switches are mainly based on electroactive behaviour. Some are discussed below;

**Rechargeable batteries:** In rechargeable batteries, conducting polymers are potentially used. This is why the conducting polymers have a commercial impact. Some leading companies like BASF/VARTA and Allied Signal are investigated conducting polymer in batteries. The conducting polymers *viz.*, polyacetylene, polyaniline Polythiophene, polypyrrole, etc have been used as electrode materials in rechargeable batteries.

**Sensors:** Because of electrical nature, conducting polymers are widely used in different sensors (chemical sensors or as gas sensors). In its simplest form of mechanism, sensor materials are absorbed, a particular vapour and affect the conductivity. The change in electrical signal may be due to the presence analytes.

**Electrochromic devices:** The device convert optical properties of a material by the action of an electric field, the phenomenon is called **Electrochromic devices**. Conducting polymers have an electronic band structure. There is a gap between two energy bands such as valence band and the conduction band. The energy gap determines the optical properties of the conducting polymers. The color changes are produced by doping. Doping is modified the conducting polymer band structure. The first electrochromic materials are used in display panels, sun energy crossing a window, automotive industry, rear view mirrors, etc.

**Electromechanical Actuators:** Actuation is one of the behaviour of conducting polymers. This means change in volume of conducting polymer by the change of their oxidation state. So, conducting polymers have ability to convert electrical energy into mechanical work.

**Drug release systems:** Conducting polymers is also used as drug release system by controlled manner. Ions can be selectively released *i.e.*, biologically active ions such as adenosine 5-triphosphate (ATP) and Heparin. The Principle used in the system is potential dependence ion transport. It is an interesting way to deliver ionic drugs to certain biological systems.

**Catalyst:** Generally, conducting polymers show redox property. So, these are expected to act as redox catalyst. The catalytic behaviour has been controlled by doping. In case of polyaniline and polypyrrole, bonding between transition metal(s) to the nitrogen atoms makes them complexes. This may possible by the interaction between transition metals and a conjugated chain. The characteristics of conjugated



polymers are expected to provide novel catalytic system.

## 5. 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.

## 6. 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 [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 [51-53].

## 7. Clay Minerals

The layered clays which can be used for the preparation of polymer nanocomposites may be divided into two types.

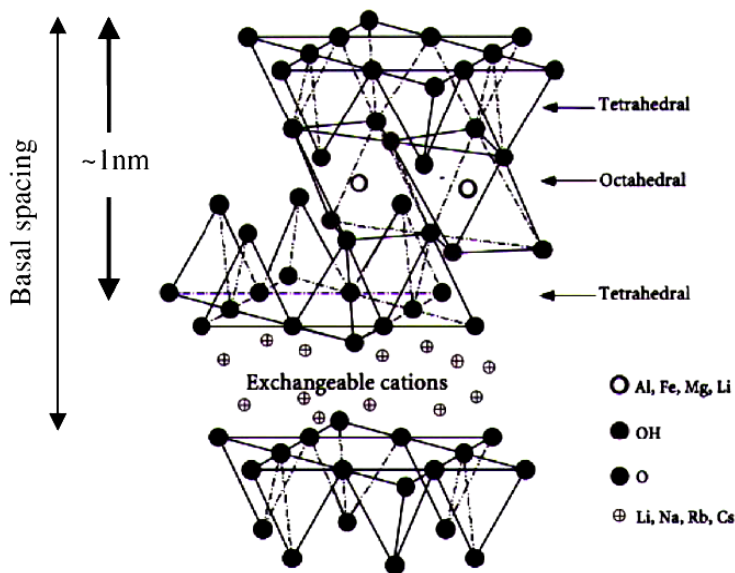


Figure 2. Schematic representation of the clay structure [51]

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

Type of clay	Formula	Origin	Substitution	Layer charge
<b>2:1 type</b>				
MMT	$M_x(Al_{2-x}Mg_xSi_4O_{10}(OH)_2nH_2O$	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	$M_x(Mg_{3-x}Li_x)Si_4O_{10}F_2nH_2O$	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
<b>1:1 type</b>				
Kaolinite	$Al_2Si_2O_5(OH)_4$	N	---	Neutral
Halloysite	$Al_2Si_2O_5(OH)_4H_2O$	N	---	Neutral
Hydrotalcite	$Mg_6Al_2(CO_3)(OH)_{16}4H_2O$	S	Octahedral	+ve
<b>Layered silicic acid</b>				
Kanemite	$NaHSi_2O_5.7H_2O$	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	$Na_2Si_{20}O_{44}.10H_2O$	N/S	Tetrahedral	-ve

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

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. 2**) [51-53].

## 8. 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**.

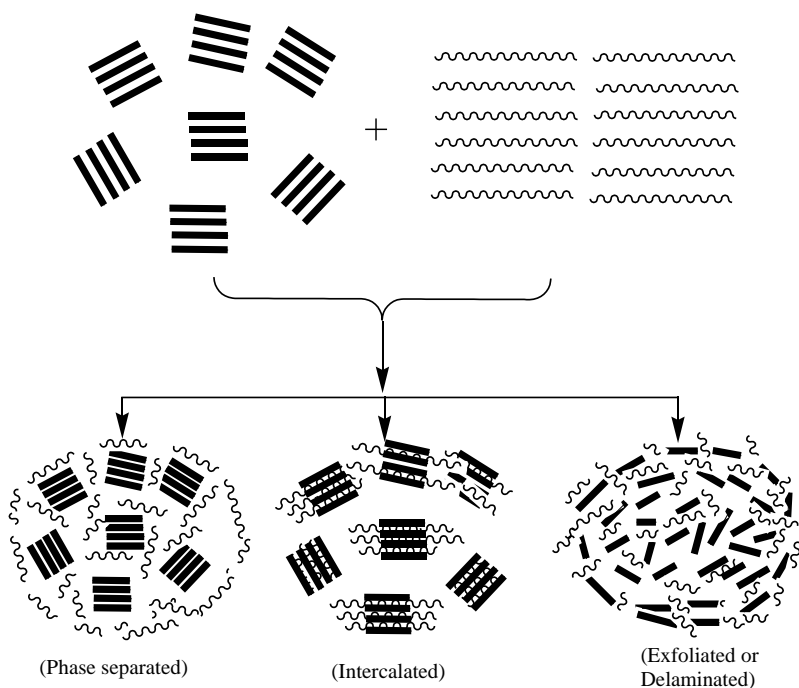
**Table 3.** Some parameters of MMT and organically modified nanoclays

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

## 9. 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. 3** shows a diagram of three broad classes of thermodynamically achievable polymer/layered silicate nanocomposites [51].



**Figure 3.** Three typical nanocomposites prepared from conducting polymer and clay minerals: (a) phase separated nanocomposite; (b) intercalated nanocomposite; (c) exfoliated or delaminated nanocomposite [51]

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

### 9.1. *Ex Situ* Nanocomposites

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

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

## 9.2. 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.

**Table 4.** Selected conducting polymer/clay nanocomposites

Polymer	Layered clay	Synthesis method	Structure of nanocomposite	Reference No.
olyaniline	MMT CdS	Emulsion	intercalation	70
		Micro-emulsion	intercalation	71
		<i>in situ</i>	intercalation	61
		<i>ex situ</i>	Not mention	61
		Chemical-oxidation	Not mention	61
	Om-MMT	Dispersion	Exfoliation/ intercalation	51
	Maghnite-H+	<i>in situ</i>	intercalation	72
	Cloisite 15A	<i>in situ</i>	Not mention	73
Polypyrrole	MMT	Chemical-oxidation		74
	Bentonite	Chemical-oxidation	intercalation	75
	Hydroxy appatite	Electropoly-merization	Not mention	76
	VMT	Chemical-oxidation	intercalation	77
Polythiophene	Modified MMT	<i>in situ</i>	intercalation	64

In this technique, different metal and metal oxide nanoparticles are encapsulated in the core of conducting polymers. *Core-shell* structured silica ( $\text{SiO}_2$ ) nanoparticles based PANI and Ppy nanocomposites were synthesized in stable colloidal forms, where  $\text{SiO}_2$  was used as the core [67]. Colloidal PPy-Au *core-shell* structured nanocomposites have been synthesized by a template-guided polymerization technique [68]. Deng and co-workers have reported the synthesis of *core-shell* structured ferromagnetic ( $\text{Fe}_3\text{O}_4$ )-cross linked PANI nanocomposites. This composite shows *core-shell* morphology in aqueous solution [69]. Layered clays, synthesis method, structure of nanocomposites of selected conducting polymer/clay based nanocomposites are presented in **Table 4**.

Hematite/silica/polypyrrole ( $\text{Fe}_2\text{O}_3/\text{SiO}_2/\text{PPy}$ ) ellipsoidal sandwich composite spheres as well as  $\text{SiO}_2/\text{PPy}$  ellipsoidal hollow capsules with movable hematite as cores and Ppy as shell were successfully fabricated by *core-shell* technique [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 [78]. Electromagnetic functionalized *core-shell* nanocomposites of polypyrrole (PPy) were prepared by a self-assembly process [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 [79]. Polypyrrole (PPy)-coated Ag composites were synthesized by interfacial polymerization process in the presence of polyvinyl pyrrolidone (PVP) by Feng *et al.* [78]. *Core-shell* nanocomposites of  $\text{CuO}/\text{PANI}$  [80],  $\text{Fe}_2\text{O}_3/\text{PANI}$  [80],  $\text{In}_2\text{O}_3/\text{PANI}$  [80] and  $\text{Fe}_2\text{O}_3/\text{SiO}_2/\text{PANI}$  [80] were successfully prepared using a double-surfactant-layer assisted polymerization method. Chuang and Yang [81] have reported the preparation of  $\text{CeO}_2/\text{PANI}$  ( $\text{CeO}_2/\text{PANI}$ ) *core-shell* nanocomposites via chemical oxidation method using aniline as monomer and  $\text{CeO}_2$  as an oxidant as well as nanomaterials. Synthesis of metallic copper nanoparticle coated with polypyrrole was very recently reported by Kobayashi *et al.* [82].

### 9.3. Solution Casting

In this technique, homogenous dispersion of organoclay ( $\text{Na}^+$  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 [83].

## 10. Solubility of Polyaniline

### 10.1. 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 [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 [85], such as N-methyl pyrrolidone (NMP), dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), m-cresol, chloroform ( $\text{CHCl}_3$ ) 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 increase 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) [86].

## **10.2. Substituted Polyanilines**

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 [87], alkoxy [88] groups, phosphoric and sulphonic acid [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 [87] or electrochemically [87]. The major drawback of these rings substituted PANIs is the fact that solubility is achieved at the cost of conductivity [87].

## **10.3. Functionalized Protonic Acid As Dopant**

Cao, Smith, and Heeger [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 ionically bound to the oppositely charged protonated PANI chain, and the 'tail' is chosen to be compatible with non-polar or weakly polar organic liquids [90]. This is called 'counter-ion' induced processability.

## **10.4. Blends Of Polyaniline**

Conducting blend is another kind of conducting materials, which supports to improve the solubility and that, is found from literatures [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 [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 [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 [92], polyamides [95],

poly (vinyl alcohol) [96], poly (vinyl chloride) [97], and so forth have been extensively studied.

## **10.5 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 [89,88].

## **11. Polyaniline Dispersions**

Dispersion polymerization is a well known technique for the synthesis of conventional polymer in both aqueous and non-aqueous media [18,98,99]. Colloidal dispersion is one of the widely used and technologically important ways for tackling the problem of poor solubility of PANI [100,101]. Dispersion of PANI is used in the preparation of blend with thermoplastic polymers [47].

## **12. Polymer Stabilized Polyaniline Dispersions**

Various polymeric steric stabilizers such as ethyl cellulose [102], carboxymethyl cellulose [103], poly (vinyl alcohol) [96], poly (vinyl methyl ether) [104], poly (N-vinylpyrrolidone) [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 [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 [102]. The possible synthetic routes and the properties of PANI colloids have been reviewed by Stejskal [102]. The morphology and the size of colloidal particles are strongly depended on the steric stabilizer, oxidizing agent and reaction conditions [106]. On the other hand, the use of polymeric stabilizers in PANI drastically lowers the electrical conductivity of PANI [107].

## **13. 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 [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 [108]. These polymers are self-doped Polythiophenes. The electrochemical polymerization of aniline carboxylic acid isomers has been recently reported [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 [110]. Electro-co-polymerization of aniline and o-aminobenzenesulphonic acid formed sulfonated PANI which was soluble in neutral pH [111].

Introduction of sulphonic acid group to the PANI chain makes soluble PANI which is self-doped and is known as Sulfonated PANI (SPAN). By chemical and electrochemical method, methoxyaniline sulphonic acid is polymerized [112-114]. Another type of conducting PANI was synthesised for improving the processability as well as redox-activity over a wide pH range [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 [118], naphthalene sulphonic acid [119], polyethylene oxide (PEO) [120], water soluble polymers such as poly (N-vinyl pyrrolidone) [121], organic dopants [122] and silica colloids [123].

Polyanilines can also be formed using aniline as monomer and polyelectrolytes such as polystyrenesulphonic acid [124], polyacrylic acid [125] and poly (2-acryloamido-2-methyl-1-propane sulphonic acid) [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 [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) [126]. The use of these non-conducting polyelectrolytes resulted in low electrical conductivity of the water dispersible PANI [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 [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 [131].

## **14. 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 [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.

## 15. Gas Sensor

Gas sensor plays an important role in the monitoring and controlling the environment for detection of test gas/analytes present in the environment. The detection of test gas is very important in today's life in many different sectors like industrial, medical, environmental, and domestic to detect toxic and flammable gases [133]. The specific applications of gas sensors are presented in **Table 5**. It provides early warning against harmful agents present in the environment for safety [133]. Without sensors, significant advances in industrial and environmental monitoring, control and instrumentation will not be possible. Hence, the development of reliable and economically fabricated devices is essential. Directly, this allows to sense these species with high efficiency and rapid analysis, which help the mankind for healthy life. The interaction between the test gas and the sensor surface can be detected measurement of change in resistance, capacitance, work function, mass, optical characteristics, etc.

**Table 5.** Specific applications of gas sensors in different areas

<b>Application Areas</b>	<b>Purpose of Gas sensing</b>
Indoor air quality monitoring	Cooking gas leakage monitoring, air quality control, monitoring heat ventilation and air conditioning (HVAC) system
Human safety	Inflammable and toxic gas detection, smoke detection, hydrogen detection in aerospace, methane leak detection, detection of explosive materials
Food industries	Monitoring microbial, fungal attack of food, packaging quality control
Automobile industries	Fuel to oxygen ratio determination, car ventilation system control, NOx detection, HVAC control
Health care	Breath analysis, disease detection

Environment may contain corrosive or contaminating species, which can seriously interfere with sensor operation and ultimately it reduces the sensor performances. Accordingly, sensor technology has continued to achieve adequate sensitivity, selectivity, reproducibility, and stability at reasonable cost [134,135].

Gases are key targets in many industrial and domestic activities requiring the precise measurement or control. This has been stimulated by a series of clean air laws, which have or are being legislative on the international, national, state and local levels. To meet these demands, the sensitivity, selectivity and stability of conventional

sensors need to be drastically improved. To achieve these goals, attention is being focused on several approaches such as research on novel sensing materials, use of catalysts and promoters, surface modification of sensor, multi-sensor array systems, data processing methods (FFT and wavelet transform, pattern recognition), fabrication techniques, optimization of sensor performance with the use of nanotechnology.

Conducting polymers are of increasing importance in the development of sensors due to their potential nature. These are room temperature operation, low fabrication cost, ease of deposition onto a wide variety of substrates and their rich structural modification chemistry [136]. Among the conducting polymer family, PANI is one of the most highly studied gas sensing materials because of its simple synthesis, environmental stability and straightforward redox doping/dedoping chemistry to control conductivity [137]. PANI nanofibers possess higher aspect ratio, *i.e.*, surface to volume ratios [138] and permit easier addition of surface functionality and interaction compared with traditional PANI which is highly agglomerated. In addition, PANI nanofibers have a cylindrical morphology and form porous structures when deposited as thin films. This structure allows the diffusion of gas molecules into and out of the PANI film. As a result, most reports indicate that nanostructured PANI performs the gas sensing applications [139].

The sensitivity of conventional PANI film-based sensor depends on the film thickness [140]. On the other hand, sensitivity of a PANI nanofiber-based sensor is independent of film thickness. This is due to the porous structure of the PANI film which leads to diffuse gas molecules on the surface of sensor and dominating the sensor response. The thickness plays the important role in the fabrication of sensor and produces the reproducible responses [140]. A gas sensor can be described as a device, which upon exposure to a gas alters one or more of its physical properties (*e.g.*, mass, electrical conductivity or capacitance) in a way that can be measured and quantified directly or indirectly [141]. Structurally, every gas sensor consists of a physical transducer and a sensitive layer. Usually, the sensitive layer which is in contact with the environment is laid down on top of the transducer platform. At the sensitive layer, the gas molecules interact chemically with the surface, producing a change in physical/chemical properties. These changes are measured by the transducer resulting in the output electrical signals [142]. Gas sensors can be classified according to their operating principle or material use, each class having different parameters.

## **15.1 Types of Gas Sensor**

There are a huge number of sensors using a wide variety of methods and technologies with which gas species can be analysed both quantitatively and qualitatively. All of these methods aim to provide accurate, stable, high resolution, low cost sensing. Therefore, when selecting an approach, it is essential to account for temperature, humidity, shock and vibrations. All these factors can greatly impact on the sensors' performance [143]. Gas sensors can be classified according to the materials used on the surface of the transducer, such as metal oxide semiconductor (MOS), conducting polymer, etc.

## **15.2 Conductometric Gas Sensors**

Conducting polymers are widely used in gas sensor, based on the electrical conduction mechanism (*e.g.*, chemoresistors) [144,145]. They consist of two electrodes with the polymer film in between. They are usually operated at room temperature (low-power). Many commercialized sensors are based on this principle. The related technologies such as fabrication technique and measuring type are established. Thick films, thin films, fibers and bulk materials can be utilized as the sensing elements of a chemiresistor and the output signal is resistance or current or which are facile to measure. The chemiresistor is formed by patterning metal interdigitated transducers (IDTs) on any insulating substrate such as alumina and silicon. The chemiresistor also contains a micro-heater fabricated on the opposite side of the IDT pattern for semiconducting metal oxides. Both semiconducting metal oxides and conducting polymers are chosen for the sensing materials as their conductivity is changed in presence of specific gas molecules. Conductometric sensors have very good linearity and can measure large or small gas concentrations (ppm to ppb ranges) as well as requiring less calibration than other sensors and ability to operate in the continuous presence of a gas.

## **15.3 Conducting Polymer (Cp) Based Sensors**

Polymer based gas sensors measure resistance changes in thin film structures. Among the conducting polymer family, PANI and PPy are possibly the most studied polymers for sensor applications due to their simple synthesis, environmental stability and straightforward doping/dedoping characteristics to control the conductivity [137]. For sensing applications, the suitable polymers have conjugated  $\pi$ -electron system along the polymer backbone. However, the choice of the polymer is limited to ICPs or those which can be made conducting by doping the polymer with counter ions using reducing or oxidising processes. Conducting polymeric layers can be incorporated in many different types of transducers, including conductometric, SAW and optical transducers [146,147]. For sensing measurement, usually a thin polymer film is directly deposited onto the sensor substrate by electrochemical or chemical polymerization. Drop casting, dip and spin coating, screen printing, layer by layer self assembled and Langmuir-Blodgett (LB) technique can also be used to deposit thin films onto the substrates [147]. Conducting polymer sensors operate at room temperature. Their advantages also include high sensitivity, small size, low production costs and ease of deposition on a wide variety of substrates [148]. Disadvantages include the reproducibility of fabrication, strong humidity interference, and base line drift over time due to oxidation processes or changes in the conformation by exposure to inappropriate compounds. The sensitivity of these type of sensors can be altered over a wide range by incorporating functional side groups to the polymer backbone, the selection of doping ions, variation of polymer chain length, condition of the polymerization and the use of nanostructured forms [148]. Among these options, the nanostructured forms of polymer appear to be the most promising to develop highly sensitive and stable gas sensor.

More attention has been devoted to increase the sensitivity, response time and stability of the gas sensors by modifying the sensing materials. Varieties of conducting polymers such as PPy, PTh and PANI have been used as the active materials in the sensors and are mentioned in **Table 6**.

**Table 6.** Conducting polymer composite used in gas sensors

Conducting polymer	Second component	Texture	Reference
PPy	PS	Blend	[157]
	High density polyethylene (HDPE)	Blend	[158]
	PEO	Blend	[159]
	PVA	Blend	[160]
	PMMA	Coated	[161]
	PMMA	Coated	[162]
	Poly(etheretherketone) (PEEK)	Blend	[162]
	PVDF	Blend	[163]
	PVAc	Blend	[164]
	PVC	Coated	[164]
	Poly (acrylonitrile-co-butadiene-co-stryrene) (ABS)		[158]
PTh	4-t-butyl-Cu-phthalocyanine	Blend	[165]
PANI	PS	Blend	[166]
	PVA	Blend	[167]
	PMMA	Blend	[168]
	PVDF	Coated	[169]
	Poly (butyl acrylate-co-vinyl acetate) (PBuA-VAc)	Blend	[170]
	PP + Carbon black + Thermoplastic PU	Blend	[171]
	PS + Carbon black + Thermoplastic PU	Blend	[172]
	Ethylene vinyl acetate copolymer		[173]
	(EVA)/copolyamide (CoPA)		[174]
	Nylon 6		

The introduction of side chains to the backbones of conducting polymers has two effects. Firstly, most of the side chains are able to increase the solubility of conducting polymers. This helps to process into the sensing film by LB technology, spin coating, ink-printing or other solution-assistant method. Secondly, the functional chains can regulate the properties of conducting polymers as well as it creates space

between molecules [149] or dipole moments [150], or bring additional interactions with analytes. Because of this, it may enhance the response, shorten the response time, or produce sensitivity to other gases. Many sensors employ substituted or copolymerized conducting polymers as the active materials. Dopants can influence the physical and chemical properties of the conducting polymers. Conducting polymers doped with different ions may give distinct responses to a specific analyte. PANI doped with small inorganic ions showed a resistance increase to ammonia, while acrylic acid doped PANI exhibited an inverse response [151]. It should be mentioned that different dopants in a sensing system shows the different dopants activity. The % Response is estimated by the ratio of change of resistance ( $\Delta R = R - R_0$ ) and initial resistance ( $R_0$ ). High conductivity resulted in a low initial resistance  $R_0$  and high relative response ( $\Delta R/R_0$ ) [152]. Camphorsulphonic acid (CSA) doped PANI shows better response compared to those doped with diphenyl phosphate (DPPH) and maleic acid (Mac) for the detection of water vapor [153]. Hong et al. [154] studied the reversibility of PANI based chemiresistor, and found that strong acid dopants resulted in better reversibility, while a worse response. Differences in sensing performances between  $\text{Cl}^-$ ,  $\text{SO}_4^-$  and  $\text{NO}_3^-$  doped Ppy composites were also studied [155]. Further, de Souza et al. [156] tried to find the relationship between the response and the molecular sizes of dopants.

The functions of incorporating another component into the conducting polymers are manifold. We can classify these sensors according to sensing mechanisms. In the composites, the second components play an important role in sensing process. They may improve the properties of sensing film (*i.e.*, partition coefficient [175]), help in electron or proton transfer [176], or directly interact with analytes by swelling [177] or electron/proton exchange [177]. As well, the second components are introduced only to improve the device configuration, *e.g.*, change the morphology of the film, which is expected to influence the performance of the sensors [178,179], improve the mechanical property [180] or protect sensing film [170]. The content of the conducting polymer will also influence the performance of the sensor [181-183].

## **16. Device Fabrication**

For sensors, a thin film active layer is most suitable. However, morphology change of sensing layer can strongly influence the performances of sensor. These effects are usually attributed to be the results of changing the ratio of surface area to volume (aspect ratio) [184]. A film with higher aspect ratio makes analyte molecules to diffuse and interact with the sensing layer more easily, which lead to a higher sensitivity and shorter response time. The materials used in the device may be in the form of thin or porous film [185-187]. In porous film, the volume ratio of micropores increases and is able to enhance the response [179]. The reverse effect is insensitive to its thickness [186]. Thin film fabricated by LB technique was also used [188,189]. Other than the LB technique, spin coating, dip coating, sputtering technique were employed. Fibers, wires, tubes, etc. in nanoregime have high aspect values. So, they

are perfect candidates for preparing sensors with high sensitivities and fast responses [190-197]. Chemical modification of the surface of PANI can be done by grafting onto Si with good adherence [198]. These technologies are useful in the fabrication of electrochemical sensors.

## **17. Working Environment**

The temperature at which a sensor can perform is most important. Like semiconductors, the conductance of conducting polymers increases with the increase of temperature. For a chemiresistor, the initial conductance of conducting polymer is changed as the temperature alters [199,200]. However, the change of initial value is not the key issue. Other than the temperature, the influence of humidity, pressure, introducing hydrophobic substituted groups on polymer backbone reduces the sensor performance [201,202]. When designing a chemiresistor, the influence of current also should not be neglected. Stronger current flow through conducting polymer will produce heat, which can affect the response as described above [203].

## **18. Sensing Principle**

The proposed sensing mechanism of PANI for CH<sub>4</sub> is mainly based on the interaction phenomenon due to the presence of active sites in PANI chains. Still the mechanism is not fully clear. It is believed that CH<sub>4</sub> interacts with oxygen which is present in the environment to form H<sub>2</sub>O and the presence of H<sub>2</sub>O ruins the ability of PANI to sense the CH<sub>4</sub> [204,205]. This causes the resistance to change. It is detected by transducer by signal as resistance. Understanding the sensing properties of PANI depends on the reversible binding of the target molecule with the sensing film and the minimal interaction between sensing material and the chemical species which may be present in the sensed environment. Therefore, a molecular level understanding of the sensing mechanism can provide adequate information for the sensitivity and selectivity issues induced by analyte, moisture and temperature changes.

## **19. Measurement of The Gas Sensing Characteristics**

In *dynamic* method, the sensors are kept in a chamber with continuous flow of gases, this leads more gas molecules over the sensing surface. At elevated temperature (sensor operating temperature) first the sensor is allowed to be exposed in a continuous flow of air (usually controlled by mass flow controllers) to attain a constant base resistance in air. After achieving a fixed sensor resistance in air ( $R_a$ ) a calculated amount of test / carrier gas mixture is passed through the chamber with same flow rate until it attains a fixed resistance ( $R_g$ ). Generally the sensor recovery is attained by flushing the sensor with the flow of air. The characteristic sensor parameters and their significance are presented in **Table 7**.

**Table 7.** Characteristic sensor parameters and their significance

Sensor parameters	Significance
Response (R) (%)	$(R_a - R_g)/R_a$ % or $R_a/R_g$ where $R_a$ and $R_g$ is the resistance of the sensor in presence of air and test gas respectively
Selectivity	Maximum response to a particular gas over other test gases
Response range	The minimum and maximum gas concentration can be detected by a sensing element
Stability	Minimal variation of the base resistance (measured in ambient condition) after repeated response-recovery cycles

## 20. Advantages of Using Conducting Polymers

The advantages of using conducting polymers as the sensing layers are listed as following.

### Room Temperature Operations

For conducting polymer based sensor, the interaction between conducting polymer and gas analyte is rather strong at room temperature. Therefore, this sensor can give remarkable signals. This endows conducting polymer sensors with low energy consumption and simple device configuration.

### Facile Property Adjustment

The backbones of common conducting polymers are built up with aromatic rings, which are easy to attach various grafts through electrophilic substitutions. Both substituted conducting polymer, presence of variety of substituents and copolymerizing with different monomers, it is facile to adjust both the chemical and physical properties of conducting polymers. These are useful for promoting selectivity of sensors, and convenient in fabricating sensor arrays. Detection limits of conducting polymers and their composites used for gas sensing are shown in **Table 8**.

### High Sensitivity and Short Response Time

The detection limits are rather low for conducting polymer based sensors. For inorganic analytes such as CO, CO<sub>2</sub>, NO<sub>x</sub>, etc., the detection limit is smaller than 1 ppm, and for organic analytes (CH<sub>4</sub>, n-Hexane, etc.), the limit is found about several ppm or lower. The response times of these sensors are usually hundreds of seconds. The response obtained from ultra thin film sensors may be as low as few seconds [206-210].



## Easy Device Fabrication

The fabrication of sensors based on conducting polymers is much easier than that based on other sensing materials. Furthermore, by introducing longer side chains on conducting polymer backbone, the solubility of conducting polymers can be greatly improved, which make them to be processed into films from their solutions. The different techniques are employed for making films by casting, layer-by-layer deposition, spin-coating or LB technique.

## Long Time Instability and Irreversibility

Stability of the conducting polymer based sensors is a major issue.

**Table 8.** Detection limits of sensors based on conducting polymers and their composites to several gases

Analyte	Sensing material	Detect limit	Sensor type	Reference
NO <sub>2</sub>	PPy/PET PTh/CuPc	<20 ppm	Chemresistor	[189]
	PANI/In <sub>2</sub> O <sub>3</sub>	4.3 ppm	Chemresistor	[176]
	PANI/FeAl	<0.5 ppm	SAW	[206]
	PANI/heavy CO]	0.2 ppm	Chemresistor	[207]
	PANI/FeAl	<10 ppm	Chemresistor	[192]
HCl	PANI/In <sub>2</sub> O <sub>3</sub>	10 ppm	Chemresistor	[208]
H <sub>2</sub> S	PANI	<60 ppm	SAW	[206]
CO	PANI/Pd	< 25 ppm	Chemresistor	[209]
	Poly(3-methylthiophene)/	<1 ppm	Chemresistor	[210]
Water		Several ppm	Chemresistor	[183]
Methanol	MWNT	<10 ppm	Chemresistor	[211]
Methane halide	PANI/Cu			

The efficiency of the sensors decreased significantly as they were stored in open environment or air for a relatively long time. Many conducting polymers like PANIs are easy to be dedoped when they are exposed to air. This may be considered when designing sensing materials. Another problem is the irreversibility of these sensors, *i.e.*, the response of sensors gradually fall down in the sensing cycles, or the signal cannot return to the original value after exposed to analytes. The mechanism of irreversibility is still not clear now.

The growing areas of conducting polymer based materials are generating many exciting new materials with novel properties. It is therefore, of immense significance to explore whether nanostructures of conducting polymers can lead to better performance and whether reliable and scalable synthetic methods can be developed in order to provide the necessary materials base for both research and applications.

## 21. Conclusions

Now-a-days, conducting polymer composites are being studied extensively due to their potential applications in sensors, and actuators. For the commercial applications of polymer composites, the synthesis, and processability must be simple, direct and cost-effective, along with improved material properties. In the present work, a variety of materials, *viz.*, hydrophobic nanomaterials (Cloisite 20A), dopants such as HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> acrylic acid (AA), polyacrylic acid (PAA), substituted form of aniline, aniline, aniline hydrochloride and thermoplastic polymer as base materials (DL-PLA) are used to prepare several composites.

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