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A review on the conducting polymers

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Abstract
During last few decades, many researchers have worked and are working in the field of conducting polymers. The focus of this review is to give details of methods of synthesis and applications of doped conducting polymers in various fields like corrosion protection, bio-medical applications, sensors and electronics etc.

Keywords: bio medical, conducting polymers, corrosion, doped, electronics

1. Introduction

Approximately three decades ago, intrinsically conducting polymers were discovered and this discovery withdraw attention of researchers because of countless applications of these polymers in scientific field. These are also called as synthetic metals as their electrical conductivity is very high analogous to those of metals. The examples of various conducting polymers (CPs) are: polyacetylene, poly furan, polypyrrole, polythiophene, which are in sulaters in their neutral state [Figure 1]. The insulating behavior of polymers can be converted into conducting by carrying out doping of different salts by chemical and electrochemical redox reactions.

The highly conducting polysulfur nitride $[SN]_x$ was discovered by Walatka *et al.* in 1973 [1]. MacDiarmid, Shirakawa and Heeger enhanced the semiconducting behavior of organic polyacetylene in late 1970 which was synthesized by chemical polymerization method. Their work on doping of polyacetylene with halogen derivatives was noticed and published in chemical communication journal in 1977. These three scientists were conferred Nobel Prize in Chemistry in 2000 for the discovery of conducting polymers (CPs). After the discovery of conducting polyacetylene scientists turned interest in making of other conducting polymers like polythiophene, polyaniline, polypyrrole, polyfuran. In contrary to those of metals, these polymers can be processed at low temperatures but the main problem with these polymers is of their stability. The conducting nature of these polymers is intrinsic as it is due to its structure rather than by adding any conducting materials.

In 1987 Heeger and his coworkers used polythiophene for making of diodes for electronic devices applications and then developed high efficiency polymer based LEDs. These polymer LEDs have been used for making of emission displays which were used in cell phones in 2003 [2].

The various applications of conducting polymers can be increased by doping with other functional materials to form polymer composites [3]. These are used in different fields like physics, chemistry, electronics, and biomedical science [4].

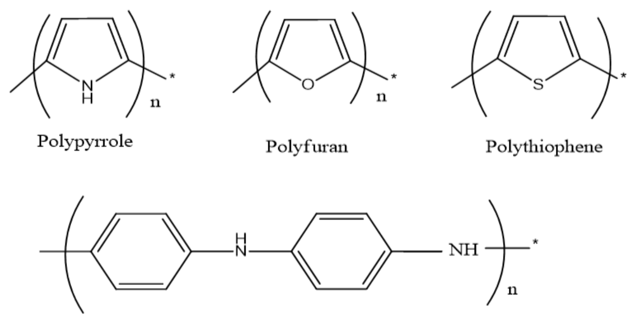

Fig 1: Examples of Intrinsically Conducting Polymers

Conducting polymers containing metal particles possess interesting properties of scientific and practical interests [5]. During past few decades, researchers are paying more attention in conducting polymer composites to develop some new properties that were not observed in individual materials [6, 7]. Researchers have more interest in development of three diamentional structure of conducting polymers, hybrid and nano hybrid materials of conducting polymers. The hybrid and nanohybrid conducting polymers are synthesized by adding metal, metal oxides, graphene, graphene oxide in conducting polymers. These new materials improve functionality in different areas like in sensors, electronic devices and in biomedical. The graphene nano hybrid of these polymers are used as electrode in synthesis of capacitors. These nanohybrid materials increase stability, flexibility and capacitances of capacitors [8]. Such polymers can be deposited either chemically or electrochemically on the metal. The different properties of polymers like thermal stability, mechanical properties, conductivity, corrosion protection properties on steel and aluminium can be improved by doping. The doped conducting polymers have more capability for corrosion protection than undoped polymers because they give suitable environment for corrosion protection on metal surfaces by restricting movements of corrosive agents or forming a uniform passive layer of doped polymers on metal surfaces [9-11].

2. Synthesis

In the available literature, different ways to produce ICP have been demonstrated. The polymerization process form a solution containing the monomer is either chemical or electrochemical process.

2.1 Chemical polymerization

In this polymerization monomers can be polymerized by various oxidizing agents like ammonium per sulphate, hydrogen per oxides *etc.* [12]. The chemical polymerization of aniline is shown in Figure 2. This type of polymerization occurs by any of the methods: Addition polymerization and step growth polymerization. An oxidant is used to polymerize the monomer and anions are doped as a counter part of the oxidative CP. This method to produce ICPs is widely used in industry.

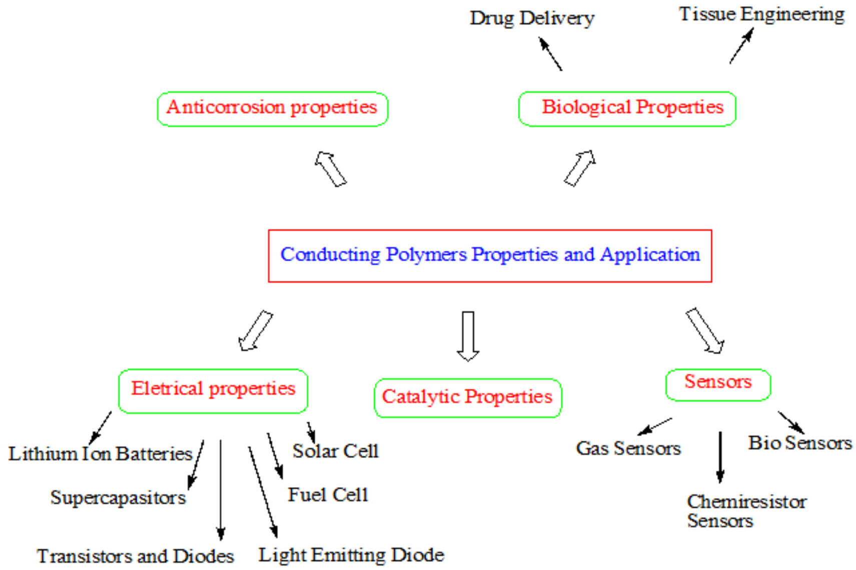

Fig 2: Reaction showing Chemical Polymerization of aniline

Polyaniline and Polypyrrole were synthesized on various substrates such as Pt, Au, Fe, Al, stainless steel, carbon fibers, brass and zinc [13-15]. Isomers of Poly-toluidine have been synthesized using chemical oxidation method at 0 ºC using potassium dichromate as oxidant and hydrochloric acid as dopant [16]. Polyaniline composites doped with TiO_2 were also synthesized by this method [17]. Polypyrrole doped with various dopants like Lithium per Chlorate ($LiClO_4$), para-Toluene Sulfonate (p-TS) and Napthalene Sulfonic acid (NSA) was synthesized by chemical polymerization [18]. Polyaniline doped with tungstate was also chemically synthesized and characterized by various techniques [19].

The composites films of polypyrrole and polyvinylidine fluoride composite films were formed by chemical oxidation method and ammonium per sulphate used as oxidant [20]. The nanocomposites of polypyrrole with copper sulfide were synthesized and characterized by various techniques [21].

Polymerization of furan by acidic catalysts has been reported by various researchers [22, 23]. Armour *et al*. observed electrical conductivity of polyfuran which was synthesized chemically by use of trichloroacetic acid [24]. Polyfuran was synthesized by using pyridinium chlorochromate (PCC) as oxidizing agent [25].

Pyrrole were polymerized by chemical oxidation method in the presence of $Fe_2(SO_4)_3$ and surfactant. The surfactant and oxidizing agent increased conductivity and yield of polypyrrole [26]. Polypyrrole doped with tungstate or vanadate were synthesized by chemical polymerization method and characterized by various techniques [27].

2.2 Electrochemical synthesis

The conducting polymers are also synthesized by electrochemical methods. It is very simple and better technique for prepartion of conducting polymers [28] because in this technique, polymerization and doping level could be controlled. In this technique three electrodes working, counter, and reference electrode are required.

The physical properties of CPs coating are affected by the nature and size of counter ions used. The properties of conducting polymers like thermal and mechanical can be improved by incorporation of sulfonated aromatic ions [29]. The coating of poly (N-methyl pyrrole) doped with TiO_2 deposited on steel substrates by this method was studied [30]. PPy/TiO_2 nano-composites were synthesized and these composites are used for paint application [31]. The electropolymerization of polyaniline, polypyrrole and their composites were carried out on stainless steel [32] and aluminium [33] by using cyclic voltammetry technique. Oxalic acid and tungstate doped polypyrrole films were potentio-statically electro-polymerized on the surface of aluminum alloy 1100 [34]. Polyaniline composites doped with tungstate [35] and molybdate [36] were synthesized by electrochemical method. Polypyrrole composites doped with zinc phosphate was deposited on AISI 1010 steel [37]. The copper doped polypyrrole was synthesized on steel by electrochemical method for corrosion protection [38].

Table 1: Comparison of Chemical and Electrochemical Polymerization

Chemical Polymerization	Electrochemical Polymerization
Yield of product is large in amount	Yield is less and synthesis of thin film is possible
Synthesis is difficult	Synthesis is quite easy.
They do not offer control of polymerization and doping level	In this method polymerization and doping level can be controlled
Doping and polymerization do not occur simultaneously.	Doping and polymerization occur simultaneously
Polymer is easily collected and packed	Difficult to remove film from electrode surface

3. Properties and applications

Conducting Polymers have wide applications in various fields such as supercapacitors, electrochromic devices, biosensors, electrocatalysts [39-41]. Conducting polymer nanocomposites of inorganic oxides have various applications in the field of chemistry and physics due to their electro-optical properties [42]. Various applications and properties of conducting polymers are shown in Figure 3. Several properties of conducting polymers like prosessibility, conductivity, permeability and mechanical properties are increased by dopant anions [43-45].

3.1 Electrical properties

Conducting polymers have various applications in electronic devices like batteries, solar cells, fuel cells, supercapacitors due to highly conducting nature of polymers.
Various applications of CPs are described below.

Lithium ion batteries

Conducting polymers have been used in batteries. Several polymers like polypyrrole, polyaniline, polyacetylene are used as electrodes in batteries. PPy composites doped with $MnCo_2O_4$ are used as anode in lithium ion batteries. These composites have good stability, high performance rate and light weight [46]. These batteries are used in electrical vehicles, mobile phone, tablets.

Solar cells

Conducting polymers have been used in solar cells. These are used as an electro catalyst in solar cells. PPy aluminium oxide composites were used as electro catalyst for solar cells. Dye sensitized and photovoltaic solar cells based on conducting polymers are used in the place of silicon solar cells because these have high energy conversion efficiency, low cost than silicon based solar cell. These are also used as energy transfer mediators in solar cell [47].

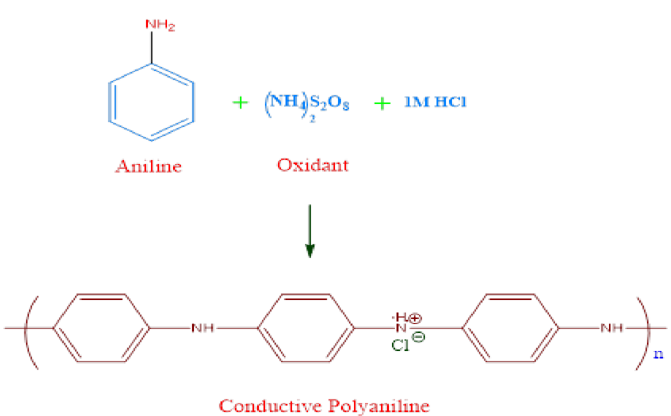

Fig 3: Applications and Properties of Conducting Polymers

Fuel cells

In past few decades, fuel cells have various advantages for applications in electric vehicles, automobiles [48]. Polymer fuel cells are of two types: low temperature and high temperature fuel cell. The membrane of high temperature fuel cells made with poly (benzamidazoles). Direct methanol fuel cells (DMFCs) have been used in the field of energy applications. Because they have fuel portability and high energy conversion efficiency [49]. Conducting polymers with 1D-nanostructures used as electro catalyst supports in cells [50].

Ligth Emitting Diodes (LEDs)

Conducting polymers like Poly(p-phenylenevinylenes) (PPVs), Poly(dialkylfluorenes) (PFs), Polythiophenes (PThs) and their derivatives exhibit potential for polymer light-emitting diodes (PLED) applications [51, 52]. By introducing bulky phenyl side groups in the polymer, performance of PLED could be improved [53, 54].

Supercapacitors

These are energy storage devices and used in solar arrays, hybrid electric vehicles. They have intermediate specific energy between batteries and capacitors. They have high charging and discharging capability. The supercapacitors based on conducting polymers have high charge storage efficiency so they can store large amount of energy [55]. Conducting polymers have been used as active electrode materials for supercapacitors due to high conductivity, flexibility, stability and low cost [56-58]. Hybrid type supercapacitor is shown in Figure 4.

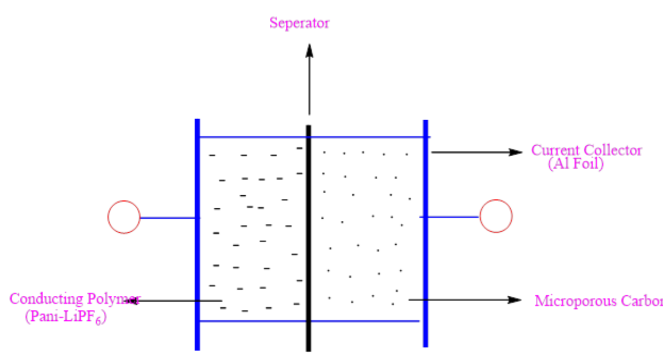

Fig 4: Hybrid type supercapacitor [59]

3.2 Anticorrosion properties

These days conducting polymers and their composites have been used as corrosion protecting agents on metal surfaces [60-61]. Corrosion protecting behavior of these composites is due to capacity of inhibit the movement of corrosion causing agents on surface of metals [62-64].

It was studied that the polyanilne coating on steel surface protect from corrosion by the formation of passive film [65]. Polyaniline epoxy blended coating on steel as corrosion inhibitor have been studied [66]. Polyaniline/polypyrrole and polyaniline-polypyrrole phosphotungustate composites were used as corrosion protecting agents on mild steel surface. Composite films give better corrosion protection then bare polyaniline and polypyrrole [67]. Polyaniline doped with TiO_2 nanoparticals (PTC) were used as corrosion protectors and they were more effective than undoped Polyaniline [17].

Oxalate and tungstate doped PPy were used as corrosion protector on aluminium was observed [34]. It was observed that the PANI–MoO_4^{2-} coating acts as better corrosion inhibitor as compared to pure PANI coating [36]. Polyaniline and its composites films possess corrosion inhibition properties [68, 69]. It was studied that zinc phosphate doped PPy gives better corrosion protection than undoped PPy [37]. Poly-6-amino-m-cresol doped with copper nanocomposites give corrosion protection of mild steel. These composites give better performance than bare polymer [70]. The corrosion behavior of 7075 aluminum, copper modified Al, polypyrrole modified Al and copper /polypyrrole modified Al samples were noticed.

3.3 Catalytic properties

Conducting polymers have been used as electrocatalyst and photocatalyst in biosensors, cells and energy related devices because of high conductivity and electroactive properties of conducting polymers. The high conductivity of conducting polymers increase the efficiency of charge transfer between electrode and electrolyte which improve catalytic activity. These are used as catalyst for enzymes in electrochemical sensors. The nanocomposites of polymers were used as photo catalysts [71]. The nanocomposites of polypyrrole–titanium dioxide showed more photocatalytic activities in degradation of Rhodamine B than pure TiO_2 [72]. Fe_3O_4/Pd@PPy composites showed superior catalytic activity and better stability in successive cycling tests [73].

3.4 Sensors

Conducting polymers have wide applications in sensors like gas sensors, bio sensors, optical sensors and chemiresistor sensors.

Gas sensors

Conducting polymers are used in gas sensors. These are used in forming of active layer in sensors due to conductive and flexible nature of conducting polymers. Gas sensors have wide range of applications in different areas like industrial production, food processing, environmental monitoring and health care *et al* [74-76]. Conducting polymers and doped conducting polymers with different metal salts have been used in gas sensors. Polypyrrole film with various dopants has been used in gas sensors [77-78].

Bio sensors

Conducting polymers are very useful for the expansion of biosensors because these are good materials for immobilization of biomolecules. Conducting polymers and their composites are used in fabrication of different biosensors and also improve speed and sensitivity of biosensors. Delocalization of electrons in conducting polymers is very fast which is good for efficient biosensors [79]. The conducting polymers provide suitable environment for immobilization of enzymes and biomolecules on electrode surface. The enzymes and biomolecules may be amalgamated in conducting polymer films during electrochemical deposition on electrodes. The amalgamation of enzymes in conducting polymers gives proximity between active site of the enzyme and conducting surface of the electrode making it suitable for biosensor construction. Glucose oxidase can be successfully amalgamated in polypyrrole films for glucose detection [80]. The biosensors based on conducting polymers were discovered for the treatment of penicillin and detection of innumerable chromosomal disorders. Highly sensitive and rapid flow injection system for urea analysis was fabricated using composite film of polypyrrole and a polyion complex [81]. Glucose biosensors are used for the estimation of glucose by arrest of glucose oxidase enzymes with conducting polymers. The DNA biosensors based on conducting polymers have been investigated for diagnosis and treatment of various diseases like chromosomal disorder by repairing, degradation or multiplication. Biosensors have great role in environmental monitoring by controlling various hazardous chemicals like formaldehyde, hydrogen peroxide which causes pollution in environment [82].

Chemiresistor sensors

The conducting polymers have also been used in chemiresistor sensors due to their conductivity. The conducting polymers play an important role in sensors because they can be act both electron donor or electron acceptor when interect with gaseous form. The conductivity of conducting polymers increases when it act as electron donor to gas and decreases when it act as electron acceptor to gas [83]. Pt, Au and Pt-Ni IDAs pre-patterned over alumina, quartz, glass, acrylic strip, silicon chips, Si_3N_4/Si are normally used as chemiresistor sensors [84].

3.5 Biomedical applications

Conducting polymers have innumerable applications in the field of medical science like drug delivery, biomedical implants, tissue engineering and diabetic monitoring.

Drug delivery

During last few years conducting polymers have been used in drug delivery due to biomedical compatibility. These are good for drug release applications [85]. The choice of drug delivery method depends upon the types of drug and types of treatment required. The routes of drug delivery are peroral, gastrointestinal, rectal, ocular, intravaginal, transdermal, vascular injection, nasal and pulmonary [86]. The different types of drugs like anionic, cationic or neutral can be injected in to polymer backbone [87].

The surface area of conducting polymer films can be increased by titanium and carbon nanotubes for storage of drugs [88, 89]. Many therapeutic drugs, such as 2-ethylhexyl phosphate, dopamine, naproxen, heparin, and dexamethasone have been bound and successfully released from these polymers [90, 91].

Tissue engineering

Conducting polymers also find applications in tissue engineering due to their stimulus-responsive property. The composites of these polymers act as substrates which promote cell growth, adhesion, and proliferation at the polymer-tissue interface [92].

Diabetic monitoring

Conducting polymers and their nanocomposites have advantages in the diagnosis and treatment of diabetes. These are used for manufacturing of devices which needs in diabetes treatment of human being. The advantages of using conducting polymers in diabetes because physical and chemical properties of conducting polymer can be modified by doping with different chemical agents as required. The glucose biosensor which is used in treatment of diabetes. Conducting polymers are applied in closed loop delivery devices which needs for diabetic paitents [93].

4. Conclusion

This paper gives information about the chemical and electrochemical methods of synthesis and applications of conducting polymer in different fields like electronic devices, sensors, protection of corrosion, drug delivery and tissue engineering. The nanocomposites and nanohybrid materials of conducting polymers improve the useful properties of polymers in different fields.

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