

Synthetic Evaluation of Cobalt Doped Nano Structured Polyaniline Conjugate Polymer

D.M Nagrik¹, R.S. SURALKAR², S.R Ingle³

¹Assistant Professor G.S Science, Art & Commerce College, Khamgaon,

²Assistant Professor, Pratap College Amalner

³Associate Professor, Jijamata Mahavidyalay, Buldhana

Abstract

For more than three decades, conducting polymers (CPs) have piqued the curiosity of scientists due to their many advantages over other materials, including their greater stability, reduced weight, easier processing, corrosion resistance, and enough electrical conductivity. Rechargeable batteries, electrochromic display devices, light-reflecting or light-transmitting appliances for optical information, sensors and storage for glare reduction systems and smart windows in automobiles and buildings, polymeric light emitting diodes (PLEDs), photovoltaic devices, transistors, electromagnetic shielding against electro-magnetic interferences (EMI), and printed electronic circuits are all examples of CPs' applications. Using PANi/BC composites with conjugated backbones was considered to increase thermal stability. Because BC was able to compensate for PANi's rigidity and brittleness, it might be a good substrate for it. The electrical conductivity of PANi/BC composites reached up to 3.8×10^{-1} S/cm when 0.32 M aniline was utilised in the interfacial polymerization. It is possible that this PANi/BC nanocomposite may be used in biocompatibility and electrical conductivity applications, such as in biological and chemical sensors.

Keywords: *Conducting Polymers, Synthesis, PANI, EMI.*

1. INTRODUCTION

Conjugated polymers have gained increased interest because of their unusual electrochemical, optical, and mechanical characteristics. Polyaniline (PANI) is the most desirable conjugated polymer because of its controlled doping levels and extensive uses, including anticorrosion coating, sensors, reduction of hazardous in water, and tissue engineering. Although the solubility in common solvents is relatively low for PANI made in the standard approach utilising aniline, an oxidant, and a small molecule acid, its uses are limited. Adding insult to injury, since the thermal breakdown temperature is lower than the melting temperature, the conjugated polymers can't be processed using the usual melting methods used for ordinary thermoplastics. There has been a significant amount of study on conducting polymers since the discovery that conjugated polymers may be made to conduct electricity by doping. Non-redox acid/base doping may be used to adapt the properties of Polyaniline to particular uses. A change in any one of these processes would influence the conductivity of polyaniline, which is a polymer with a high conductivity because it is able to transfer charge carriers down its backbone and hop between polymer chains.

2. LITERATURE REVIEW

Caroline Duc et.al (2016) Sub-ppm amounts of hydrogen sulphide gas (H₂S), which may be found in both natural and man-made environments, are dangerous because of the gas' pungent odour and the potential for poisoning. This gas's danger has been monitored and controlled in real time by scientists for decades. They've been designing sensors with strong metrological qualities and good stability. Alternatives to the most prevalent methods, such as electrochemical and optical sensors, include chemiresistive sensors based on conductive polymer. In terms of design and performance, they have a number of benefits to offer. Various materials and sensing techniques have been evaluated in this study to provide an overview of the progress achieved in developing conductive polymer sensors for H₂S detection. These sensors have certain limits, and we highlight the most promising ways for enabling their usage in real-world applications.

FAHAD USMAN ET.AL (2017) Using Ammonium peroxydisulfate, oxidative polymerization of aniline (PANI) has been used to create PANI/chitosan, PANI/reduced graphene-oxide, and a ternary composite of the three materials (APS). FTIR, XRD, FESEM, and UV-VIS methods were used to verify that the synthesis had been completed successfully. For example, complex refractive index, complex dielectric constant and optical

conductivity were measured in the UV, Vis and NIR region for PANI and its composites. Sulphur and the absorbance values of the polymers were shown to have a significant impact on the outcomes. The lack of research on the optical properties of p-toluene sulfonic acid-doped polyaniline and its composites might thus serve as an initial answer to the shortage of such studies.

ANJU YADAV ET.AL (2015) The in-situ emulsion polymerization of aniline in aqueous DBSA solution led to the formation of PANI nanorods doped with dodecyl benzene sulphonic acid (DBSA). In addition to XRD patterns, UV-Visible Spectroscopy, and FTIR analyses, FESEM pictures show that PANI and PANI-DBSA were formed. To create a porous gas sensing active layer, a chloroform dispersion of synthesised PANI-DBSA was spin coated over a prefabricated interdigitated Pt patterned glass substrate. The sensor has a reaction time of 6 s, a recovery time of 37 s, and a relative response value of 9.57 in the range of 1-1200 ppm ammonia concentration. As a result, it showed a 0.01675 relative response per ppm value for ammonia concentrations between 1 and 50 parts per million (ppm).

YUMEI ZHANG ET.AL (2018) Polyaniline nanospheres with high molecular weight (Mw 48,000) and nanofibers with low molecular weight (Mw 4000) were made and cytotoxicity, acute oral toxicity test, and histopathology investigation were carried out. At greater concentrations, both nanofibers and nanospheres were shown to be highly toxic to BV2 microglia cells, with nanospheres being more hazardous. After ingesting the drug, there was no immediate toxicity. When administered at a dose of 100 mg/mL, polyaniline nanofibers did cause some liver damage, as seen by the results of the histopathology section. The findings showed that the lesser the toxicity, the larger the molecular weight. It is possible to make polyaniline with a larger molecular weight in order to make it biocompatible. Results improved our knowledge of polyaniline nanomaterial's biocompatibility and made it more useful in the medical area.

KRUSHNA J KSHIRASAGAR ET.AL (2017) Pd-PANI nanocomposite (NCs) is generated in surfactant-based liquid crystalline mesophase by chemical oxidation and radiolysis. Polymerization of aniline monomers and their 1D development into polyaniline (PANI) nanowires are made easier by utilising ammonium persulfate to limit the liquid crystalline mesophase. Typical PANI nanowire diameters range from 30 to 40 nm. Because of the palladium (Pd) nanowires' homogeneous size distribution, the in situ radiolytic reduction of palladium ions is essential. Structures of PANI with diameters of 30–40 nm are seen in the nanocomposites, which are adorned with Pd nanoparticles of 10 nm in diameter. A remarkable degree of stability in the liquid crystalline mesophase is suggested by the PANI nanowires' equal average diameter before and after gamma irradiation.

3. CONDUCTING POLYMERS

A conducting polymer is an organic polymer that may either be a conductor or a semiconductor, depending on how it is characterised. PANI, PANI, PANI, PANI, PANI, PANI, PANI, PANI, PANI, and PANI are the most often researched organic polymers. They have special optical and electrical characteristics because they are conjugated, which means that electron delocalization occurs along their polymer backbone.

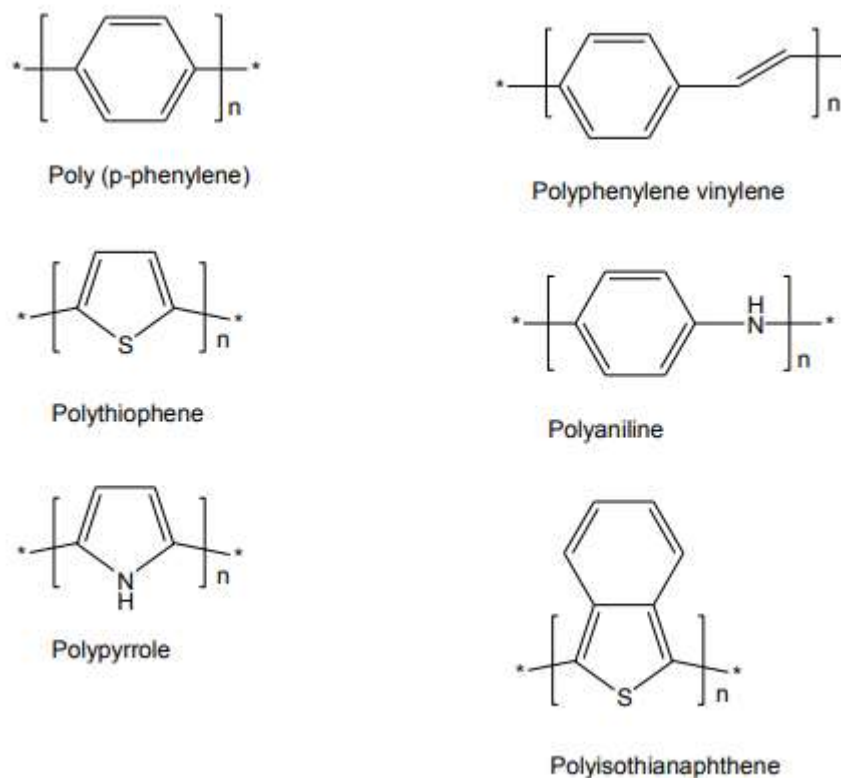


Figure 1. Typical (shown uncharged) structures of conducting polymers

4. POLYANILINE

Runge discovered polyaniline in 1834 and referred to it as aniline black. As a result of this, Lethe conducted study in 1862 to examine this substance. Reduced benzoid units combine with oxidised quinoid units to form the polymer PANI, which is classified as a mixed oxidation state polymer. It was found by Green and Woodhead (1912) that polyaniline had this fascinating feature. It was also observed that PANI possessed properties that allowed it to flip between conducting and insulating. Since then, the material has been a major focus of study in academic circles.

5. STRUCTURE OF POLYANILINE

A mixed oxidation state polymer, PANI's average oxidation state is $1-y$, wherein the value of y determines the presence of each one of the three unique PANI oxidation states seen in Figure 2. As a result, PANI may be divided into three distinct forms: completely oxidised pernigraniline (PE), half oxidised emeraldine base (EB), and fully oxidised leucoemeraldine (LE). Due to its great stability at ambient temperature, EB is considered to be the most usable form of polyaniline. EB is formed of two benzoid units and one quinoid unit that alternate and it is known to be a semiconductor.

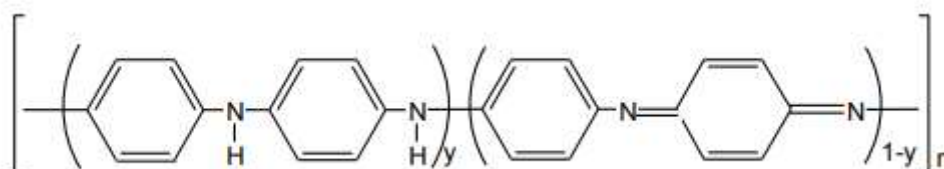


Figure 2. Different oxidation states of polyaniline ($y = 1$: leucoemeraldine, $y = 0.5$: emeraldine and $y = 0$: pernigraniline)

Emeraldine salts may also be produced via a non-redox reaction in an acidic media (ES). PE degrades far more quickly than LE does, on the other hand.

6. SYNTHESIS OF POLYANILINE

In order to make conducting polymers, a variety of approaches may be used, including electrochemical oxidation of the monomers and chemical synthesis. It's also worth noting that unusual techniques like photochemically induced polymerization and enzyme polymerization are also used in certain cases. Monomers serve primarily as starting materials for the polymerization process, which yields low molecular weight oligomers. The low molecular weight oligomers are further oxidised to form a polymer at potentials lower than those at which the monomers are oxidised. By cycling between a potential window that allows for oxidation of the monomers, the polymer may be electrodeposited onto an appropriate substrate in electrochemical polymerization. An ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ chemical oxidant is used in chemical synthesis, and the polymer precipitates out of the reaction solution. Electrochemical and chemical polymerization are the main topics of the present review, which will be expanded upon.

7. CONDUCTIVE MECHANISM

Inherent Molecular Structure

As a general rule, the energy band theory has been used to delineate the essential distinctions between semiconductors, conductors, and insulators. Energy difference between lowest unoccupied molecular orbital (LUMO) in conduction band and highest-occupied molecular orbital in valence band (HOMO) in material is known as the band gap (E). The conduction band and the valence band overlap in conductor materials, allowing electrons to easily migrate and distribute between the two bands. However, the narrow band gap of semiconductor materials allows them to conduct electricity under certain excitation situations. A substance is an insulator when the band gap is too big for electrons to traverse (no electricity is transmitted). Despite the fact that conjugated polymers are organic materials, the energy band hypothesis fails to explain why they can conduct electricity. Researchers have studied the molecular charge transport processes of conjugated polymers from both theoretical and experimental evidences. Figure 1.1 depicts the most widely recognised method, which is based on polyacetylene's high electrical conductivity and simple chemical structure. As a general rule, conjugated polymers include interchanging single and double bonds in the polymer backbone. As the name suggests, the localised σ -bonds in these connections are capable of forming strong chemical bonds. In addition, each double bond has a delocalized π -bond, which is weaker than the σ -bond, but it is still there. Electrons may effortlessly traverse the carbon backbone thanks to the overlap between orbitals in the chain of conjugated π -bonds. Conjugated π -bonds may conduct electricity as a consequence of this. But because of a particular disorder in the polymer matrix, conjugated π -bonds aren't considered to be able to turn conjugated polymers into high-conductivity materials. Charge transport in polymers is slowed down by structural and morphological abnormalities that prevent π -electrons from delocalizing.

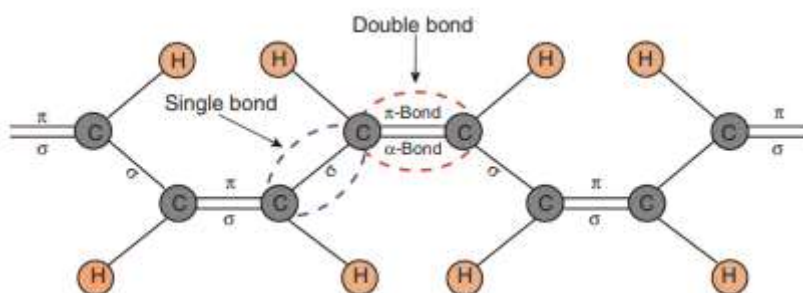


Figure 3 Scheme describing the conjugated π -system in cis-polyacetylene.

Doping and Band Structure Evolution

Pristine conjugated polymers have a conductivity between 10^6 and 10^{10} S/cm, making them an insulator-semiconductor hybrid (Figure 1.2). Doping, on the other hand, allows us to fine-tune their conductivities. When conjugated systems are doped, structural and morphological disorder may be eliminated. Solitons, polarons, and bipolarons are formed when doping is applied, reducing lattice distortion. Because of this, the conductivity of

the pure system may be increased to semiconducting or even metallic levels by doping the polymers. Tsukamoto et al. found that iodine-doped polyacetylene has a conductivity of around 10^4 S/cm, which is higher than the conductivity of lead at ambient temperature (4.8×10^4 S/cm). It has becoming more common for conjugated polymers to be used in practical applications due to their high conductivity.

There are several ways to introduce impurities into semiconductors in order to alter their conductivity, and doping is one of them. The kind of doping and conductivity of semiconductor materials are determined by the quantity of valence electrons of the impurity, namely, the dopant. As an example, the outer shell of a silicon atom is filled with four electrons. For the silicon crystal lattice, this results in either negative (a free electron, p-type doped) or positive sites (a hole, n-type doped) when phosphorus or boron (each with three valence electrons) replace silicon. They act as carriers of electrical charges and increase the silicon crystal's conductivity by up to 10^6 S cm⁻¹. Polymers have a unique doping mechanism due to the π -conjugated system, which is not present in typical semiconductors. Delocalized charges are formed on polymer backbones as a result of electron transport in conjugated polymers, which is a partial redox reaction. Adding or withdrawing electrons from the conjugated polymer chain is the primary function of the dopant. If you want to understand its workings you need to understand how electrons are added or removed from valence and conduction bands (oxidation).

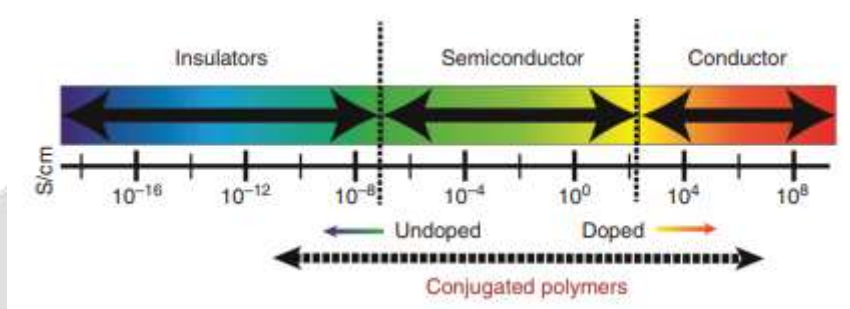


Figure 4 Conductivity range of conjugated polymers based on doped/undoped states

8. CONCLUSION

To obtain nanofibers with desired qualities, one may manipulate the polymer solution, the needle, and the collector used in electrospinning by manipulating these parameters. In addition to template coating, another method for improving PANI's processability is the addition of polymer blends and fillers to the solution.

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