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Conducting Polymers A Comprehensive Review On Recent Advances In Synthesis, Properties And Applications

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Abstract: Polymers are usually associated with the insulators, every person in the world grows up learning not to touch an electrical cord that is frayed you might receive a shock from the exposed conductive metal wire. We all know that plastics do not conduct electricity and can be used to insulate the electrical wire and protect us from electrical current. Most of us regard polymers (plastics) as being useful as a light weight replacement for heavier structural materials such as steel and wood. They are traditionally used as insulators to prevent an electric shock from a live electrical conductor. That polymers, usually associated with insulators, can be very good conductors was a quite unexpected discovery that certain polymers could be made to conduct an electrical current as efficiently as metallic copper came as a surprise to many, and was awarded the 2000 Nobel Prize in Chemistry. (The award was given to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa.) They always need some ―doping‖ with ionic components; however the resistivity can be exceedingly low. The availability and low cost of polymers like polyaniline make the field of conductive polymers a thriving industry. Conductive polymers have found their way into many other fields

Index Terms - Polymers, Conductivity, Resistivity, Doping, Polyacetilene, Polyaniline.

1.INTRODUCTION

Conducting polymers are extensively studied due to their outstanding properties, including tuneable electrical property, optical and high mechanical properties, easy synthesis and effortless fabrication and high environmental stability over conventional inorganic materials. Although conducting polymers have a lot of limitations in their pristine form, hybridization with other materials overcomes these limitations. The synergetic effects of conducting polymer composites give them wide applications in electrical, electronics and optoelectronic fields. An in-depth analysis of composites of conducting polymers with carbonaceous materials, metal oxides, transition metals and transition metal dichalcogenides etc. is used to study them effectively. Here in this review we seek to describe the transport models which help to explain the conduction mechanism, relevant synthesis approaches, and physical properties, including electrical, optical and mechanical properties. Recent developments in their applications in the fields of energy storage, photocatalysis, anti-corrosion coatings, biomedical applications and sensing applications are also explained. Structural properties play an important role in the performance of the composites.

Electrical properties of polymers are usually related to dielectric and electrical conductivity. A good conductor is a material that allows the flow of current and the insulator is the material which opposes the current. Most of the pristine polymers act as insulators except the conducting one owing to the lack of ionic or electronic pathway and covalent nature of the polymers. The addition of different conducting nanomaterials into the polymer matrices introduces interesting electrical properties to the polymers. The incorporation of graphene sheet can offer percolated pathways for electron transfer in the nanocomposite, which makes the nanocomposite electrically conductive. Now a day the world is crowded out by Copper, Aluminium as a good conducting material of electricity, because of the importance of low resistivity, good mechanical strength, resistance to corrosion, ductility and many more, low resistivity in the list of requirements is much larger now than it was in the past. And the Superconductors are in a class of their own. All kinds of materials may become superconducting at low temperatures, and there are neither general rules telling you if a material will become superconducting, nor at which temperature. If you see around you, will found that the production of metals or extraction of pure metal is a very complex and lengthy process as well as costly also. Every person in the world grows up learning not to touch an electrical cord that is frayed or you might receive a shock from the exposed conductive metal wire. We all know that plastics do not conduct electricity and can be used to insulate the electrical wire and protect us from electrical current. Most of us regard polymers (plastics) as being useful as a lightweight replacement for heavier structural materials such as steel and wood. They are traditionally used as insulators to prevent an electric shock from a live electrical conductor. That polymers, usually associated with insulators, can be very good conductors was a quite unexpected discovery that certain polymers could be made to conduct an electrical current as efficiently as metallic copper came as a surprise to many, and was awarded the 2000 Nobel Prize in Chemistry.

1.2. WHO AND HOW IT DISCOVERED?

In the year 2000 the Nobel Prize in Chemistry was awarded to three men from the field of conductive polymers. The award was given to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa. Heeger is Currently a professor of Physics at the University of California Santa Barbara and has done pioneering research in the area of semiconducting and metallic polymers and was appointed Chief Scientist of UNIAX Corporation in 1999 the company which he founded in 1990. MacDiarmid Professor of Chemistry at the University of Pennsylvania ―co-discoverer of the field of conducting polymers, more commonly knew as
―synthetic metals‖ was the chemist responsible in 1977 for the chemical and electrochemical doping of polyacetylene‖.

1.3. BAND STRUCTURE FOR CONDUCTORS, SEMICONDUCTORS, AND INSULATORS

Polymers are organic macromolecules, a long carbonic chain, composed by structural repeat entities, called mer. These smallest unit, for instance, are bonded by covalent bonds, repeating successively along a chain. A monomer, molecule composed by one mer, is the raw material to produce a polymer. The majority of polymers are insulators, due to an unavailability of free electrons to create the conductivity. In a covalent bond, showed in figure 1, the electrons are locked in these strong and directional bonds(see more at [a] of "Links" Section), so when an electric field is applied, electrons cannot drift. Therefore, these type of materials do not show a high conductivity.

The poor conductivity of polymers is also explained by the band theory (see more at [b] of "Links" Section). This theory says that the energy levels of electrons can occupy are grouped in allowed bands and may have energy levels of electron that are forbidden, denominated band gap, as shown in figure 2. This theory is resulted of Schrödinger’s Equation applied in a periodic field of a crystal solid. The lowest bands are called valence bands and are inert on an electrical perspective. On the other hand, the highest bands, which participate in the electric conduction, are called conduction bands.

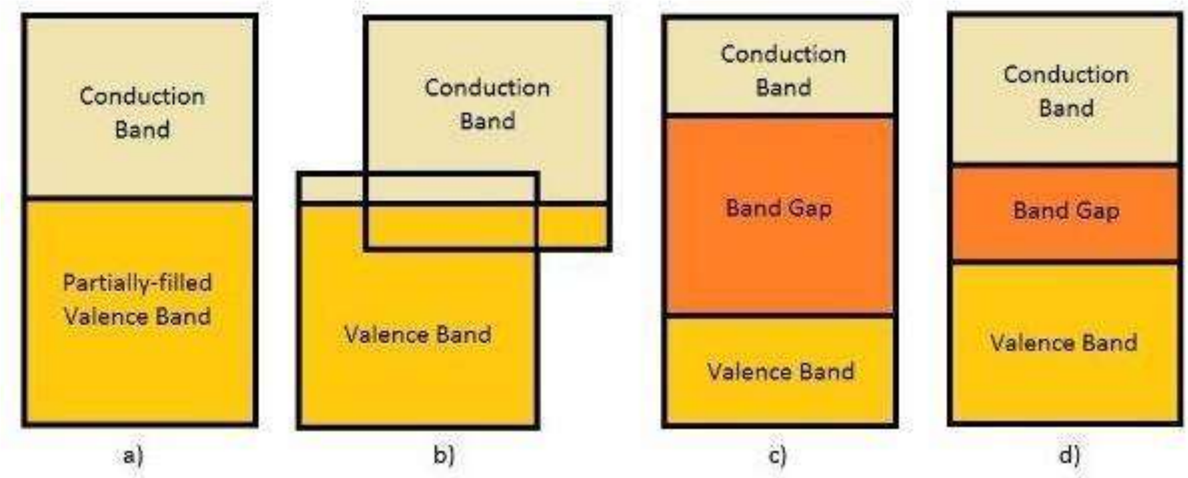

Fig. 1.3. Band Structure for Conductors, Semiconductors, and Insulators:
a) for monovalent metals; b) divalent metal; c)Insulators; and d)Semiconductors

Some conductors has a partially filled valence band that is relatively easier to excite an electron to a higher energy level, as in a). Other conductors, such as divalent metals represented in b), can have an overlap of the empty conductive band with a totally filled valence band. For semiconductor and insulators, represented in d) and c) respectively, the valence electrons must cross the band gap in order to result a conduction. The difference is a semiconductor has a relatively smaller band gap energy than insulators have . For a long period of time, polymers were considered as insulators. Until, in 1970, when the first intrinsic conductive polymer was produced by Shirakawa, Heeger, and MacDiarmid, which resulted in the Nobel prize in 2000. The polymer was produced by the exposure of the polyacetylene to dopant compounds: oxidizing or reducing agents; electron-donor or electron-receptor of electrons.

1.4. CONDUCTIVE POLYMERS

An electric current results of the orderly movement of charges in a material as a response of forces that act on them, when a voltage is applied. The positive charges flow in the direction of the electric field applied, whereas the negative charges move in the opposite direction. In the majority of materials, a current is resulted by the flux of electrons, known as electric conduction (see more at [c] of "Links" Section).

The structure of these materials has conjugated chains, that is, an alternating single and double bond between the atoms. The process of doping of conductive polymers becomes easier due to these conjugated bonds. In this process, defects and deformations in the polymeric chain are formed. An electron-deformation pair, or also an electron-phonon cloud pair, is called polarons, which is responsible by the conductivity in polymers. Bipolarons and solitons, other types of quasi-particles, also participates in the conductivity mechanism. The type of soliton, bipolaron, or polaron formed depends on the dopant used. Their meaning and the physics behind that is beyond the scope of this subject.

The charges resulted the doping process in conductive polymers is the reason of their great conductivity. The constant movement of the double bonds to stabilize the charge in the neighbor atoms causes, therefore, the movement of the charge, resulting in the conductivity. This movement of double bonds is called resonance (see more at [d] of "Links" Section) and it describes the delocalized electrons within a molecule. A delocalized electron is an electron, presented in a π bond, which is shared by three or more atoms (see more at [e] of "Links" Section). Due to this process of the polaron formation, there is a change in the band structure of the conductive polymer. It creates the polaronic conduction bands, allowed bands in the band gap, reducing the band gap energy, making the polymer able to conduct, as shown in figure

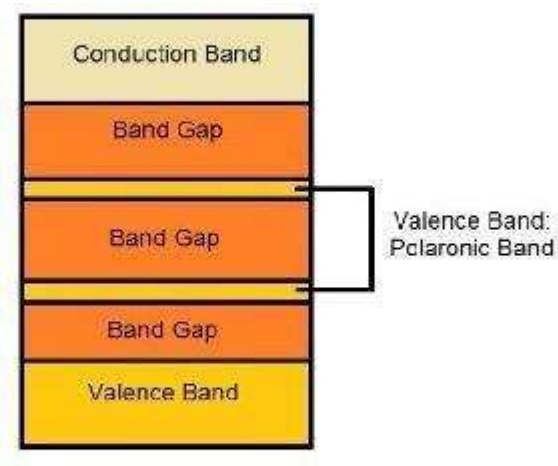

Fig. 1.4. Band Structure of a Conductive Polymer

Since the conductivity of a conductive polymer is due to the charge formed by the dopant, as the doping level increases, more charges are formed in the polymer and, thus, results in a greater conductivity. The conductivity of a conductive polymer is also temperature dependent, because as the temperature increases the molecules becomes farther from each other. Thus, the doping effect is more effective and, consequently, the amount of charges, which is the doping level of the polymer is greater, increasing the conductivity. Moreover, as the temperature increases, the energy of an electron is related with the temperature by the Boltzmann relationship. Because of that, the greater the temperature, the greater is the energy of the electrons, and, consequently, the easier is to excite the electron to the conduction band. The best-known and most studied conductive polymers are polyacetilene, polyaniline, and polypyrrole due to their wide range of applications.

1.5. POLYACETYLENE

Polyacetylene is an organic polymer with the repeat unit C_2H_2 .The polymer consists of a long chain of carbon atoms with alternating single and double bonds between them, each with one hydrogen atom. Schematically the structure of polyacetylene is shown below.

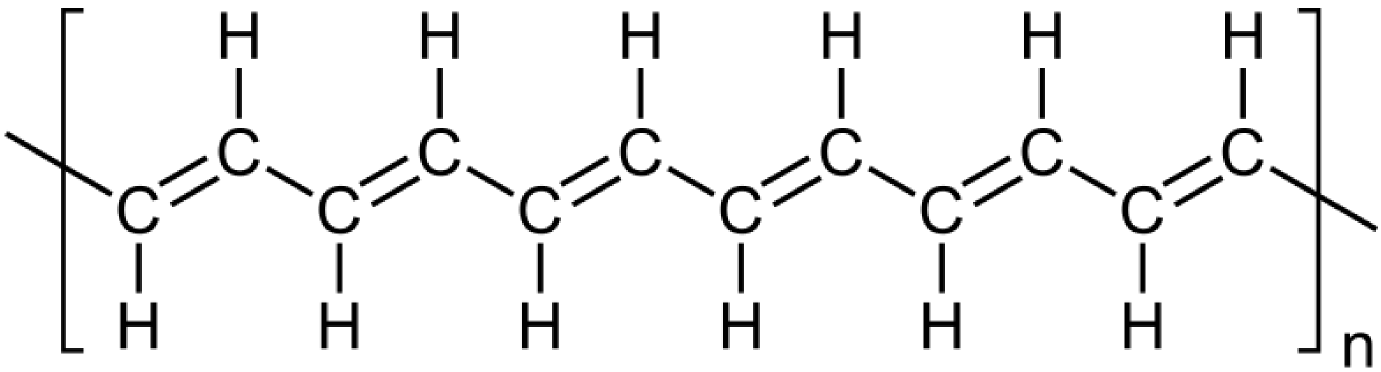

Fig. 1.5. Polyacetylene structure

Polyacetilene is one of the polymers in the study that resulted in the Chemistry Nobel prize in 2000. The polymer is synthetized by the reaction of the etyne, as commercially known as acetylene, with Ziegler-Natta catalyst. The resulting structure is shown below. The polyacetilene is the simplest polymer that shows a great value of conductivity. The anternating double and single bond in the polymer structure is what gives the polymer the ability of resonate. As dopants are inserted in the polymer, the chains of polymers presents charges. The movement of these charge, by resonance when a field is applied, gives rise to the conductivity of the material.

1.5 POLYANILINE

Polyaniline is one of the most promising conductive polymers and, therefore, one of the most studied ones. This polymer, in fact, is a family of polymers that is classified by aromatic rings bonded together by nitrogen atoms. Its structure is composed by x units of reduced species alternated with 1-x units of oxidized species, as observed in figure 6.

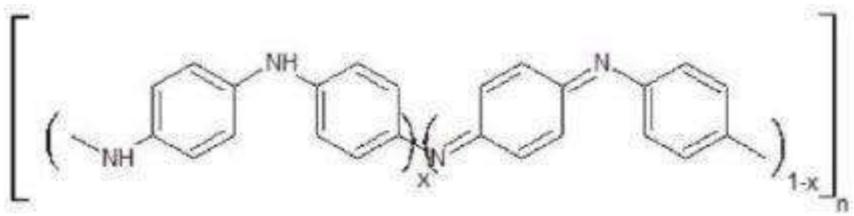

Fig. 1.5. Chemical Structure of the Polyaniline

The doping process occurs through the protonation of the nitrogen atoms in the amine groups of the polyaniline by an acidic solution, oxidizing the structure. Thus, positive charges are formed in the polyaniline structure that moves as the structure resonates, shown in figure 7.

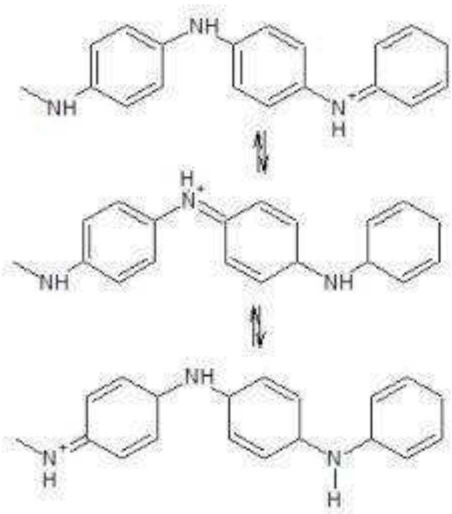

Fig. 1.5. Resonance Mechanism of Polyaniline

As the material is doped, charges appear in the structures that are stabilized by resonance, resulting in conductivity.

1.6. POLYPYRROLE

The polypyrrole is one of the conductive polymers studied in the research that resulted in the Nobel prize. It is obtained by the oxidization of the pyrrole, resulting in the structure shown below.

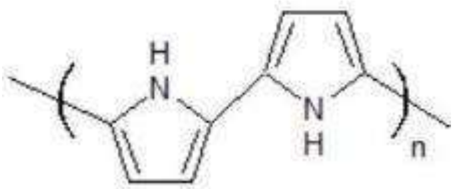

Figure 1.6. Chemical Structure of the Polypyrrole

The Redox process of the addition of an anion to the structure that is responsible to the conductive properties of the polypyrrole. Again here, the resonance occurs to stabilize the carbocation, moving the charge, resulting in conductivity, mechanism similar as shown for the previous polymers.

2. SYNTHESIS

There are three ways to produce conductive polymers: reactional chemistry, electrochemical, and photoelectrochemical, being the first one the most used, due to its high profitability and efficiency. The chemical process consists in the union of monomers by the addition of the oxidizing or reducing agents that makes the neutral polymer to a cationic or anionic ionic complex, ending the reaction by the bonding of this complex to the counter-ion of the redox agent. This process requires a high control, since the reaction is very exothermic and emits gases, requiring proper treatment and equipment of protection. The electrochemical method consists in the electronic deposition of the polymer in the electrode. The solution that the electrode is immersed has the monomers and the dopants. When a voltage or a current strong enough is applied, the monomers oxidize resulting in the polymerization. This process results in polymers with shape of the electrode, requiring a posterior processing to get the shape desired. The photoeletrochemical process is based on photoexcitation of the polymer or in compounds that have catalyst properties in presence of light, oxidizating the monomers resulting in a polymerization. Even though this process is simple and environmentally friendly, the mechanical properties of the resulting polymer is not good.

3. ELECTRICAL AND ELECTRONIC PROPERTIES

The electrical properties of a material are usually explained using its electronic band structures. The energy difference between the conduction band and the valance band classifies materials from insulators to conductors. Intrinsically conducting materials have a decreased bandgap, and the conduction and valance bands overlap. The electronic band theory clearly explained the case of conducting polymers, but some other studies have also revealed the transport properties of conducting polymers rather than band theory. All conducting polymers have conjugate bonds in their backbones, and these bonds are responsible for the movement of electrons: i.e., a single bond contains a localized σ bond and a double bond has both σ and weaker π bonds. The dual relationship between first and second carbons includes a π bond and this π bond transfers to the second and third carbons, and the π bond between the third and fourth carbon transfers to the next pair; this displacement of π bonds allows the electrons to flow.4 The conductivity shows drastic changes depending upon the dopant material, the arrangement of the polymer chain, and its length. The dopant concentration and pH value enhance the conductivity; for example, polyaniline shows excellent conductivity if the pH is maintained between 0 and 3.

3.1. CONDUCTIVITY

Conductivity and how it relates to polyacetylene will now be examined. Conductance is the reciprocal of resistance (R^- 1), where R is defined by Ohm’s Law. The resistance is proportional to the length (1) of the sample and inversely proportional to the sample cross-section A in Ohmic materials (R—pl/A). Resistivity is defined by (p), its inverse is conductivity.

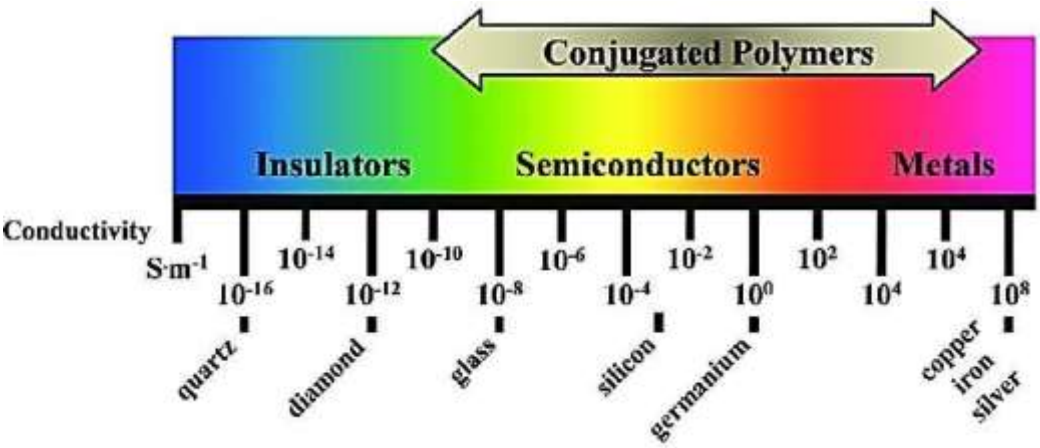

Fig. Conductivity
Silver = 1.59 x 10^{-8}, Copper = 1.72 x 10^{-8}, Aluminium = 2.82 x 10^{-8}

Unfortunately semiconductors, linear polyene chains, like polyacetylene generally deviate from Ohm’s law. Conductivity depends on the number density of charged carriers and how fast they can move in the material; it also depends on the temperature. For semiconductors conductivity generally decreases with lower temperatures.

Conductivity of a stretched polymer like polyacetylene depends on direction and may be anistropic (properties such as strength and optical and electrical properties). The conductivity of ―stretched oriented polyacetylene is some 100 times higher in the stretched direction than perpendicular to it‖ Polyacetylene has alternating single and double bonds that give rise to mobile pi electrons that when doped become highly anistropic metallic conductors.

3.2. OPTICAL PROPERTY

The electronic structure of conjugated polymers is anisotropic and quasi-one-dimensional due to the presence of π bonds in the polymer backbone by utilizing electron–phonon interactions. The electronic transport behavior in organic semiconductors is usually due to the influence of charge mobilizers like solitons, polarons, or bipolarons in the ground state degeneracy. The sub-gap optical transitions occur in the polymer backbone while doping triggers charge mobility by a shift of oscillator strength from π to π*. These nonlinear excitations are responsible for the charge mobility. The conjugated polymers behave like semiconductors in their pristine form, and they act metallically when doped with p and n dopants. In the nonlinear excitation of conjugated polymers, there are some conflicts with the photoexcitation of conjugated polymers, i.e., polarons or bound neutral excitons. Before understanding the optical property of conjugate polymers, we need to know the basics of the physical properties of simple solids. The optical constants of solids give a complete idea of both vibronic and electronic properties, when an electromagnetic wave interacts with the polymer.

3.3 MECHANICAL PROPERTIES

The mechanical properties of polymer materials depend upon the monomer arrangement and crystallinity. A crystalline polymer has better mechanical properties compared with amorphous semi-crystalline polymers. The macroscopic mechanical property of conducting polymers depends upon the microscopic change in the molecular mobility of macromolecules. Molecular mobility depends upon factors like the structure of branching polymer conformations and macroscopic properties like pressure– temperature etc. In the case of amorphous polymers, the distribution and arrangement of monomers are random, and crystalline polymers are not stacked. The molecular motion is higher in amorphous polymers, and when temperature reaches Tg the polymer is transformed to a rubbery state from its glassy state. This transition leads to a change in mechanical properties. The mechanical property of a polymer depends heavily upon the molecular weight: i.e., the toughness and strength parameters are related to molecular weight and chain entanglement.

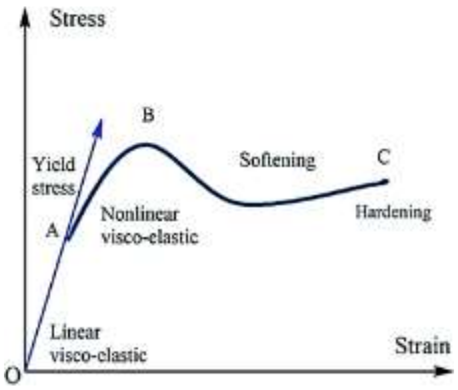

Fig 3.3.1. Graph Stress strain

4. DRAWBACKS OF METAL

Extraction Process

1. Copper and other conducting metal can be found in high-grade ores.
2. Found at particular places.
3. Mining is costly.
4. And when you treat too much of ore you will get very small amount of metal. Corrosion

Corrosion is the major problem associated with metal even though numbers of methods (Painting, varnishing) are developed to avoid the corrosion we are loosing greater percentage of metal due to corrosion. And ones the metal get corroded then it will be of no use. We are loosing about 65%of metal per year.

Low Flexibility, High Weight etc.

5. ADVANTAGE OF POLYMER

Extraction Process. Extraction of polymers is Easier than the metal, because polymer can be manufactured artificially in laboratory in bulk. Only raw material cost is considered.

Corrosion Polymers are having high resistance to corrosion and therefore atmospheric conditions do not affect it. Also polymers are non porous and does not absorb moisture. Automatically further problems are avoided.

High Flexibility, low weight. Polymers are light in weight as compare to metal.

Polymers are more flexible than any metal by nature. They offers following,

1. Machine flexibility - The different operation types that a machine can perform.
2. Material handling flexibility - The ability to move the products within a manufacturing facility.
3. Operation flexibility - The ability to produce a product in different ways.‖
4. Process flexibility - The set of products that the system can produce.

6. APPLICATIONS

This type of materials has generated interesting in many field of study, due to its conductivity properties as a metals, but remaining its relatively inert and good mechanical properties. There are many applications of these materials in electronics, such as batteries, sensors, and microelectronics devices. The polypyrrole and polyaniline are currently used in protection of metals, as an anti-corrosive coating. In the medical field, the conductive polymers can be used in the production artificial muscles, biosensors, and drugs controlled-release agents. The world economy plays an important role in the utilization of fossil fuel sources, natural gas, and coal. The depletion of fossil fuels is causing a lot of social and environmental problems. Due to climate change, global warming, and health issues, the replacement of conventional energy sources is mandatory. Because of this, scientists have put their effort into developing eco-friendly, high-energy, renewable energy resources, including supercapacitors, fuel cells, and wind energy. Nowadays, supercapacitors are of great commercial interest because of the future markets for wearable devices, electric vehicles, etc. The main difference between conventional capacitor and supercapacitor devices is that they store 1000 times more energy than a dielectric capacitor. Also, they have a high-speed charge–discharge cycle, and they exhibit high energy and power density and also good cycle life

7. FUTURE PROSPECTS AND DEVELOPMENT OF RESEARCH

The conductive polymers have a widely range of application, but in some of them the use of the metals is the better option. This is due to their high conductivity obtained by a cheaper process. Thus, the application of these materials will occur where their differential properties are useful, such as the weightless properties of polymers and their application in electronics will result in increasingly smaller and compact devices. The shielding of the electromagnetic interference and radiofrequency is also a likely market where the conductive polymers can have an easier acceptability. With the development of muscles using conductive polymers, the research about its biocompatibility will be promising in the future. The scientists also investigates the effects of doping levels, temperature and band gap in the material in order to determine the best levels to get the better conductive polymer.

8. CONCLUSION

To date, there have been a lot of studies done on the fabrication of conducting polymers. The main aim of this review article has been to explore current trends in the synthesis, properties, and applications of conducting polymers. Conducting polymers and their composites are always in the limelight because of their metallic conductivity when doped and excellent physical properties. From literature reviews, it was observed that conducting polymers in their pristine form behave as an insulator or a semiconductor. They show metallic conductivity only when doped with a suitable dopant or when made into a composite with foreign materials. The physical and chemical properties of conducting polymers also depend on morphology; different morphology gives distinguishable properties. Understanding the basic properties is essential for the design of conducting polymers for various applications. The complex structure of conducting polymers and their derivatives poses a difficulty for theoretical modelling; therefore, an understanding of the origin of conductivity and the doping mechanism is essential. Charge carriers are developed on a polymer backbone either when added to or extracted from the delocalized π bond. Various parameter s like temperature, dopants, and structural properties have an effect on transport properties.

Conducting polymers are widely used as supercapacitor electrode materials because of their metallic conductivity, flexibility, processability, and ease of fabrication. Most conducting polymers exhibit high specific capacitance, and they deliver energy rapidly. The main disadvantage of conducting polymer-based supercapacitors is their cycle life; symmetric conducting polymer supercapacitors have a lower cycle life than carbonaceous material-based supercapacitors. From the literature, we can observe that the cycle life problem can be overcome by irradiation, sonication during synthesis or compositing with carbonaceous or non- carbonaceous materials. In the case of an asymmetric configuration, conducting polymers and their derivatives as positive electrodes and carbonaceous material as negative electrodes provide a higher cycle life and specific capacitance. From the literature, we can find that stability and cycle life can be improved by incorporating metal oxides, transition metals, transition metal dichalcogenides, and carbonaceous materials. From these studies, we can understand that future developments and research should be carried out into a hybrid conducting polymer composite that will prove effective in achieving better supercapacitor performance. Among conducting polymers, polyaniline and polypyrrole have been effectively used for electrochemical sensing applications. Nanostructures of conducting polymers have great prospects in sensing action because of their high surface area or high surface to volume ratio for the diffusion of analyte gas molecules into and out of the polymer matrix, compared to their bulk form. The conducting polymer morphology and film thickness play an essential role in the sensing action because of inter-domain spacing, and this will reduce the interaction of analyte gas with the polymer. Polyaniline has better sensing behavior than the others due to its reversible doping mechanism. Hybrid conducting polymers overcome the drawback of selectivity and the high working temperature problem of metal oxide chemiresistors. Polyaniline and polypyrrole conducting polymers, and their combinations, should be explored more for the detection of oxidizing and reducing gases. Future developments should focus on other conducting polymers.

REFERENCES

1. Conducting polymers: a comprehensive review on recent advances in synthesis, Namsheer Ka and Chandra Sekhar Rout RAC Advances journal Issue 10 2021
2. T. Nezakati , A. Seifalian , A. Tan and A. M. Seifalian , Chem. Rev., 2018
3. A. J. Heeger J. Phys. Chem. B, 2001
4. Handbook of Conducting Polymers , T. A. SkotheimDekker, New York, 1986, vol. vol. 1–2,
5. T. H. Le , Y. Kim and H. Yoon , Polymers, 2017,
6. Organic Electroluminescent Materials and Devices , S. Miyata and H. S. Nalwa, Gordon & Breach, Amsterdam, 1997
7. Handbook of Organic Conductive Molecules and Polymers , H. S. NalwaWiley, New York, 1997, vol. vol. 1–4,
8. E. T. A. Skotheim , R. L. Elsenbaumer and J. R. Reynolds , Handbook of Conducting Polymers , Dekker, New York, 1998
9. G. Marsh Mater. Today, 2001,
10. J. Liu , J. W. Y. Lam and B. Zhong Tang , Synthesis and Functionality of Substituted Polyacetylenes , 2010.
11. M. Charles Acc. Chem. Res., 1995,
12. A. G. MacDiarmid , W. E. Jones , I. D. Norris , J. Gao , A. T. Johnson , N. J. Pinto , J. Hone , B. Han , F. K. Ko , H. E. Okuzaki and M. Llaguno , Synth. Met., 2001
13. Q. Tang , J. Wu , X. Sun , Q. Li and J. Lin , Langmuir, 2009