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## RESEARCH ARTICLE

### CONDUCTIVE POLYMERS FOR FRONTIER APPLICATIONS-AN OVERVIEW

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#### ABSTRACT

Polymeric materials have been gaining increasing importance over the past. This is due mainly to the flexibility in regulation of characteristics of polymers at our convenience. At times, these materials compete with numerous metals and alloys in critical sectors like aerospace and defence owing to their easy processibility and lighter in weight. However, these sectors do not involve polymers in their parent state rather as composite polymers and nanostructured polymers. Even though polymers suffer from the inferior strength and high temperature resistance, yet they are regarded to be the most sought after materials when the properties electrical resistivity, and good oxidation resistance are counted. However, some of the industrial applications call for good conductivity, easy manufacturability, and better recyclability. In these regards, conductive polymers have been synthesized of recent to serve the purpose to become front liners in meeting the requirements of industry sector. The current paper critically emphasizes the background, classification, applications and characterization of polymers. Later, detailed study on conductive polymers is done where in the mechanism of conduction, characterization, and fabrications of conductive polymers are discussed at length. Ultimately, appropriate conclusions are drawn basing the review conducted.

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#### INTRODUCTION

The term polymer in Greek means 'many parts' (Poly- "many" and mer-"part"). A polymer is a material consisting of macromolecules which essentially is a combination of many repeating subunits. Usage of polymers is versatile, because of their broad-spectrum of properties. From the strand of our DNA which is a naturally occurring biopolymer to polypropylene which is used throughout the world as plastic, polymers are found all around us. May it be natural or synthetic; polymers are created via polymerization of many small molecules known as monomers. Many classes of polymers are Composed of Hydrocarbons. Hydrocarbons are organic compounds that are made up of only two kinds of atoms, carbon and hydrogen. Few examples of polymers composed of hydrocarbons are polystyrene, polybutylene, polypropylene and so on. The Figure1 below illustrates the structure of polystyrene. There are also other polymers which have other elements rather than carbon in its backbone, Nylon is an example for such polymers which have nitrogen atoms in the repeated units.

**Background:** In 1500's, Mayans are assumed to be the first to find an application for polymers. The term polymer was framed by Jöns Jacob Berzelius in the year 1833. Charles Good year discovered vulcanization in the year 1839. In 20<sup>th</sup> century, Leo Baekeland created the first synthetic polymer which is Bakelite. In 1922, Hermann Staudinger proposed that polymers are covalently bonded macromolecules. In 1917, M Polanyi discovered chemical structure of cellulose by using X-Ray Crystallography which led to establish the fact that polymer unit cells contain sections of long chain molecules. The production of vinyl-chloride had begun in the year 1927. Polystyrene was invented in 1930, Nylon in 1938 and Polyethylene in 1941. In 1976, Polymer industry overtook steel as the nation's most widely used material per unit volume.

**Classification of Polymers:** Polymers have complex structures, vast applications and exhibit different behavior. Therefore polymers cannot be classified under one category, so they are classified based on the following considerations.

**Natural Polymers:** Natural polymers are those which are obtained naturally either by addition or condensation polymerization. Polymers are found on large-scale in nature. For example, DNA and RNA which are very important in the life process of all living organisms.

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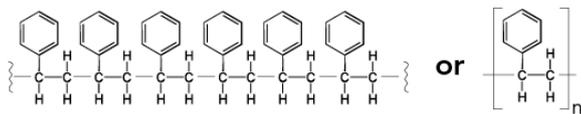


Fig. 1. Polystyrene [1]

Protein and peptides, Starch, Cellulose, Latex and Collagen are other examples for natural polymers. The Figure 2 below illustrates the structure of cellulose.

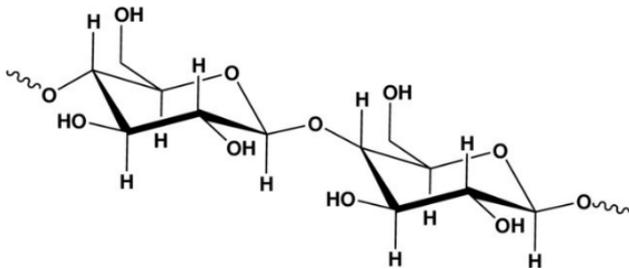


Fig.2 Polymer structure of cellulose [2]

**Semi-synthetic Polymers:** These polymers are derived from but they undergo chemical modification. For example, Cellulose is chemically modified by strong nitric acid, sulfuric acid and water into cellulose nitrate. The structure of cellulose nitrate is shown in Figure3.

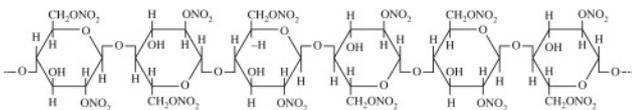


Fig. 3. Structure of cellulose nitrate [3]

**Synthetic Polymers:** Synthetic polymers are synthesized in laboratory and are called man-made polymers. Polyethylene, Nylon, PVC (Polyvinyl Chloride), synthetic rubbers and Bakelite are some examples of synthetic polymers. The polymer structure of Nylon 6, 6 is as shown in the Figure 4.

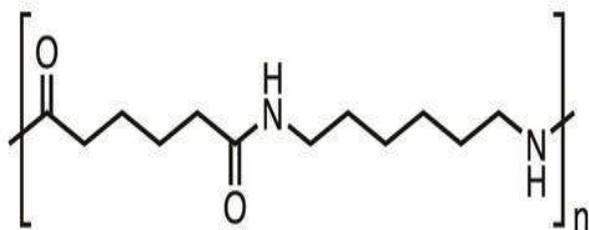


Fig.4 Nylon 6, 6 [4]

**Linear Chain Polymers:** The polymers in which monomer units are linked to form linear chains are known as linear chained polymers.

**Branched Chain Polymers:** The polymers in which monomer units are joined to form long chains with branches are known as branched chain polymers.

**Cross Linked Polymers:** The polymers in which monomer units are cross-linked together to form a 3D network are known as cross linked polymers.

The Figure 5 depicts the structure of these polymers.

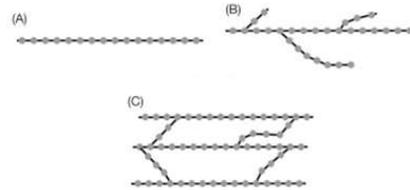


Fig. 5. A) Linear B) Branched C) Cross linked [5]

**Elastomers:** The polymers whose chains are held together by weakest intermolecular forces are called as elastomers. These forces permit the polymers to be stretched. Vulcanized rubber is an example for elastomer and is as shown in Figure 6.

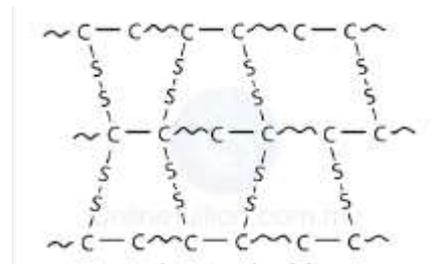


Fig. 6. Vulcanized Rubber [6]

**Fibers:** These polymers are strong, tough and have high tensile strength because of strong forces like hydrogen bonding. Nylon 66 (Figure4) is an example for such polymers.

**Thermoplastic Polymers:** These polymers have intermediate forces of attraction between elastomers and fibers. Due to which, they can be easily molded by heating. Cross-linking between chains does not exist in these polymers. Polystyrene (Figure1) is an example for thermoplastic polymers.

**Thermosetting Polymers:** These are prepared from low molecular mass semi fluid substances. Material's mechanical properties are greatly improved by these polymers. Bakelite is an example for thermosetting polymers and the structure of Bakelite is as shown in the Figure 7.

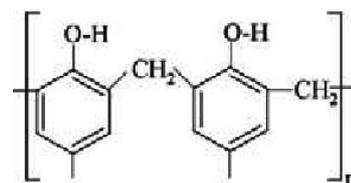


Fig.7. Chemical structure of Bakelite [7]

**Pros and Cons of Polymers:** Polymers play a significant role in the modern world. They make our lives more convenient and trouble-free in hundreds of different ways. This doesn't mean that polymers are free from disadvantages. In spite of being resistant to chemicals, polymers lack high temperature resistance. Though they are light in weight, but the weight to strength ratio is lesser than that of metals. Credits must be given to their easy processibility, manufacturability, recyclability. However, fabricating heavy structures, preventing release of toxic fumes during decomposition of the polymers limit their applications at some critical instants.

**Significant Application of Polymers:** Polymers are fabulously varied elements that have applications in aerospace, automotive, electronics, packaging, sports, textile, construction and medical industry. Commercial uses of polymers are Nylon-6 in fabric, Teflon in non-stick cookware, Bakelite in plastic switches, Rubber in making tyres, PVC in tubes and pipes and so on.

**Characterization of polymers:** Characterization sets out those features of the structure, composition and defects of a material that are important for a particular preparation, study of properties and use of the material. The characterizations of polymers have begun with the recognition and demonstration of the high molecular weight and long-chain nature of these substances. As a result of the development, many special characterization techniques for polymers and analytical methods are developed. The polymer characterization techniques are: chemical, physical, electrical, mechanical, molecular, rheological, spectroscopic, thermal property, thermal transition and viscoelasticity. All available techniques are not applicable to all polymer systems. The practical problem is not much on the availability of characterization technique, but their application in an economically feasible, scientifically sound manner.

Polymers by virtue of their weightlessness and ease of fabrication have replaced and are continuing to replace metals in several areas of applications. They are considered excellent insulators which means they have a property of trapping heat efficiently, a quality that is quite an advantage. But, this insulating property is less desired in products such as gadgets which can overheat as the coverings of it trap the heat produced by them. Once the polymers are designed, we need to characterize them. The characterization of polymers typically refers to a measure of strength, durability, elasticity, chemical inertness and electrical resistivity to evaluate their properties for physical and actual behavior (12). There are various equipments for characterization of polymers. To determine elastic modulus, ultimate stress and strain, tensile strength testing is a destructive characterization technique in which elongation is typically measured. The durability of polymers and fiber reinforced polymer composites under certain methods (13). Increase of deformation is sometimes observed when stress is applied if it is less than yield stress known as Creep. Chemical inertness is the ability a polymer can maintain its original properties after being exposed to chemical environment for a time period. The chemical inertness testing methods help to determine whether a polymer will remain functional throughout its service life or if there are issues that need to be addressed before putting a system into service. Polymers which exhibit conducting behavior can be doped to give materials with higher conductivity. To exhibit conductivity, the polymer should have linear chains such that it is highly crystalline in nature. Conducting polymers usually black maybe because of its carbon content represent an important research area with scientific problems of fundamental significance and the potential for commercial applications. Generally, polymers have poor conductivity. They can be easily oxidized and the reason to it is dopants mainly responsible for the behavior of conducting to insulating. The presence of  $\pi$  conjugation in polymers, however, confers the required mobility to charges that are created on the polymer backbone (i.e. by the process of doping) and make them electrically conductive. The effect of dopant on conductivity i.e. it increases when doping increases, mechanism of

conduction where conductivity increases as there is a rise in temperature, the effect of band gap has been studied as when there is a decrease in band gap, there is an increase in conductivity. Conducting polymers like Polypyrrole, Poly aniline and Polythiophenes and so on have been synthesized and their conductivities have been determined.

**Electrical properties of polymers:** Electrical properties of polymers, elastomers, composites and plastic films are very important to a wide range of industries such as automotive, aerospace, packaging and consumer goods. The temperature dependence of the electrical resistivity or conductivity of a polymer is a function of the molecular structure of the polymer, the nature and number of the current carriers. Electrical tests, in general, are measurements of the resistance, conductivity or charge storage either on the surface or through the material. Various factors such as dielectric constant, volume and surface resistivity are crucial to index the nature of the polymer material, specifically regarding its efficiency and conductivity. Dissipation factor measures the inefficiency of an insulating material. If a material were to be used for strictly insulating purposes, it would be better to have a lower dielectric constant. When a material is to be used in electric applications where high capacitance is needed, a higher dielectric constant is required. The test can be conducted at different frequencies, often between the 10Hz and 2MHz range - the specific frequency is determined by the customer. A sample for this test is placed between two metallic plates and capacitance is measured. A second run is measured without the specimen between the two electrodes. The ratio of these two values is the dielectric constant.

A higher dielectric strength represents a better quality of insulator. There are three basic procedures that can be used to determine the dielectric strength of an insulator. These procedures are the short-time method, the slow rate-of-rise method and the step-by-step method. Each of these three methods has the same basic set-up, which consists of the test specimen placed between two electrodes in air or in oil. The most common test, the short-time method, voltage is applied across the two electrodes and raised from zero to dielectric breakdown at a uniform rate. Breakdown is when an electrical burn-through punctures the sample, or decomposition occurs in the specimen. The rate of voltage rise is determined by the time it takes the sample to reach dielectric breakdown. The slow rate of rise method starts at 50% of the breakdown voltage as determined by the short-time-method and is increased at a uniform rate. The step-by-step method starts at 50% of the short-time-test then voltage is increased at equal increments for a specified time period until breakdown. The test is sometimes performed in oil to prevent formation of electric arc from the electrode to the ground. The recommended specimen type for this test is a 4 inch plaque or larger. Any specimen thickness can be used; however the most common thickness is between 0.8 to 3.2 mm (0.032 to 0.125 inch). Specimens over 2 mm thick are typically tested in oil to decrease the chance of flashover (high voltage electric shock) before breakdown. (14) Surface resistivity is the resistance to leakage current along the surface of an insulating material. Volume resistivity is the resistance to leakage current through the body of an insulating material. The higher the surface or volume resistivity, the lower the leakage current and the less conductive the material is. A standard size specimen is placed between two electrodes. For a few seconds, a voltage is applied and the resistance is

measured. Surface or volume resistivity is calculated. A 4-inch disk is preferable for specimen size, or a 4-inch square (14).

**Determination of conductivity of a polymer:** For the test of conductivity in polymers, it can be measured using two terminal measurements after depositing metallic contact. Few precautions are to be taken for the measurement of high resistance, which is however likely to be in polymers. Sample should be mounted in a metallic sample holder with a vacuum inside. High impedance electrometer should be used to measure current at a particular voltage. Shielded connection should be used by making measurements in ohmic range to calculate resistance and finally conductivity is measured. The simplest method to measure the conductivity of the polymer is using 4-point probe test. (14) It gives us the resistance in the sheet. Then using the resistance-conductivity formula we can calculate conductivity. Resistance is the inverse of conductance and we will be needing the film thickness to find out conductivity.

**Insulating Polymers and Conductive Polymers:** Most of the plastics are insulators (poor conductors of electricity) and resist the flow of current. Polymers are covalently bonded which makes it difficult to support the movement of electrons. Therefore they act as insulators or dielectrics. This is the most useful properties of plastic which makes them to use as switches, wire coatings and electrical and electronic products. They have wide range of electrical properties that designers of engineering components need to consider they are Dielectric strength, Volume resistivity, Surface resistivity, Arc resistance, Dissipation factor and Dielectric constant. Insulating polymers has excellent properties such as lightweight, hydrophobicity and antiweatherability.

On the other hand, there are conductive polymers like polyaniline, polypyrrole that conduct electricity. They can be semiconductors or may have metallic conductivity. In 19<sup>th</sup> century, Henry Letheby discovered polyaniline by investigating the electrochemical and chemical oxidation products of aniline in acidic media. The electrical conductivity of these polymers is based on the presence of conjugated double bonds along the polymer backbone (10). Conjugation means that the polymer backbone consists of alternating single and double bonds (10). However, the conductivity of these polymers is rather low, but when an electron is removed from the valence band by oxidation (p-doping) or added to the conducting band by reduction (n-doping) then the polymer becomes highly conductive. The conductivity of a material depends on both the density of charge carriers (number of charges per unit volume) and their mobility  $\mu$ . A relationship between mobility of the charge carriers and the electrical conductivity  $\sigma$  is as follows: If  $\mu_e$  and  $\mu_p$  are the mobilities of negative charges (electrons) and positive charges (holes) then each of these charge carriers will move with the velocity vector  $\mu_e E$  and  $\mu_p E$  in the electric field  $E$ .

The total current density is given as,

$$\sigma = e (n_e \mu_e + n_p \mu_p)$$

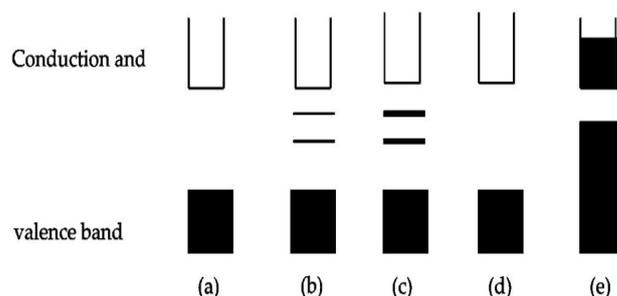
Where  $e$  = Elementary charge  
 $n_e$  = Concentration of electrons and  
 $n_p$  = Concentration of holes

The conductivity strongly depends on the temperature. For metals, it decreases with increasing temperature, whereas for semi-conductors like conducting polymers it increases (10).

**Mechanism of Conduction:** A polymer in its undoped / pure state is described as electronic insulator. When such a polymer is doped the conductivity changes from insulator to metals. The conductivity,  $\sigma$ , is proportional to carrier concentration,  $n$ , and the carrier mobility,  $\mu$  (11). The equation is given as,

$$\sigma = e n \mu \quad (1)$$

The doping of conjugated polymers generates high conductivities by increasing the value of  $n$ . This is accomplished by oxidation or reduction with electron acceptors or donors (11). The polymer is oxidized by the removal of electron and produces hole (radical cation) on the chain. The hole with lattice distortion around the charge with positive charged hole sight is known as polaron. This sight moves through the polymer and contributes to conductivity. This polymer is called p-type polymer. The n-type polymer is obtained by reduction (adding electron to the chain) and this process produces polaron with negative charge. The doping process produce carriers in polymers, but these carriers must be in mobile in order to contribute to conductivity, eq. (1). The mechanism of carrier transport in conducting polymer is probably more likely to that in amorphous semiconductors than crystalline semiconductors (11). Therefore the doping creates an active sites (polarons) which enable the carriers (electronic & holes) to move from one site to another. Concentration of dopant causes certain electrons to become unpaired and lead to the formation of polarons and bipolarons.



**Fig.9 Schematic variation of band gap as a function of doping concentration (a) undoped (b) very small doping (polaron) (c) small doping (bipolaron) (d) high doping bipolaronic band (e) 100% doping [11].**

## ADVANCES IN CONDUCTIVE POLYMERS

Conducting polymers have been widely studied to realize advanced technologies in various areas such as chemical and biosensors, catalysts, photovoltaic cells, batteries, supercapacitors, and others. They have also received special attention as promising candidates in many areas of nanoscience and nanotechnology. Hybrid nanomaterials, the combination of conducting polymers with different types of materials, such as metals and inorganic compounds have been studied most intensively. Such Nano hybrids have proven to be attractive for a wide variety of applications from organic electronics to energy storage, solar cells, and sensors. (15). The carbon nanomaterials (graphene and its derivatives) have been frequently employed as this significant investment in development is due to the recognition that nanostructured conducting polymers can play a key role in applications such

as Li-ion batteries, solar cells, sensors. In this referred article, they first classified about synthesis routes for conducting polymers as well as for hybrid nanomaterials and presented a new standard for classification. From this point of view, then the discussion was on the recent developments in synthesis approaches that have improved conventional methods. Finally, various selected applications have been reported in order to demonstrate the merits of conducting polymers.

### Fabrication of conductive polymers-challenges

Various methods have been developed to date for the fabrication of conducting polymers. The Nano hybrids mentioned are also promising candidates as they show interesting properties not observed in individual components and their bulk components. However, there are no effective methods to characterize and control the crystalline/amorphous ratio of the conducting polymers, particularly in hybrid systems (15). This might be the reason why most studies have not focused on the crystalline properties of conducting polymers for achieving metal like electrical properties. Doping is an essential step for the preparation of them. Doping consists of increasing the conductivity of certain organic polymers metallic levels by chemical or electrochemical 'pi-doping' (oxidation) or 'n-doping' (reduction). Acids such as Hydrochloric and Sulphuric are basic doping agents. Iron chloride and sulphates are considered the best oxidants. More doping techniques are employed to provide metal like conductivity and solubility. Undoped conjugated polymers state is semiconductors or insulators. In such compounds, the energy gap can be  $>2\text{eV}$ , which is too great for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophenes, polyacetylenes only have a low electrical conductivity. Upon doping, the bond alteration is diminished in conductivity increases (15).

### Recent advances in applications of conductive polymers:

The current uses for organic conducting polymers are: Organic solar cells, Printing electronic circuits, Organic light-emitting diodes (OLED), Actuators, Electrochromic, super-capacitors, chemical sensors, biosensors, Microwave-absorbent coatings, radar-absorptive coatings on stealth aircraft. There are various advantages of conducting polymers over metals, which is why metals are being constantly replaced by conducting polymers. Lighter in weight, easy and less energy consumption during processing, corrosion resistant, easily blended with other plastics, makes the material compact, most importantly, used in smart materials.

### Conclusion

An overview of polymers and the advancements in conducting polymers were elucidated in this paper. The advantages and disadvantages of polymers were discussed.

The need for insulating polymers and the mechanism of conducting polymers were illustrated. The characterization techniques and applications of polymers were narrated. The electrical properties of insulating polymers and conductive polymers were discussed. The typical applications of conducting polymers were drawn. It can be concluded that the conducting polymers replace metals in various significant applications and is used as one of the smart materials.

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