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RECENT ADVANCES IN POLYMERIC MATERIALS: A REVIEW OF FABRICATION METHODS, CHARACTERIZATION, AND APPLICATIONS

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Abstract:

Polymers are typically associated with insulators. People learn early on not to touch frayed electrical cords to avoid a shock from exposed conductive metal wires. Plastics, for instance, do not conduct electricity and are used to insulate electrical wires, protecting us from electrical currents. Polymers are commonly seen as lightweight replacements for heavier materials like steel and wood and are traditionally used as insulators to prevent electric shocks from live conductors. However, the discovery that certain polymers could conduct electricity as efficiently as metallic copper was quite unexpected and led to the 2000 Nobel Prize in Chemistry being awarded to Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa. Conductive polymers need to be doped with ionic components to achieve low resistivity. The availability and low cost of polymers like Polypayrrole have made the field of conductive polymers a thriving industry, and these materials have found applications in many areas.

Keywords: Polymers Materials, Polypayrrole, Polyacetilene, Conductivity, Resistivity, Doping, Chemical Synthesis

1. Introduction

Conducting polymers have garnered significant attention due to their remarkable properties, such as adjustable electrical conductivity, optical and mechanical characteristics, ease of synthesis and fabrication, and superior environmental stability compared to traditional inorganic materials. While pristine conducting polymers have several limitations, these can be mitigated through hybridization with other materials. The synergistic effects of conducting polymer composites make them highly suitable for applications in electrical, electronic, and optoelectronic fields. A comprehensive analysis of these composites, which include carbon-based materials, metal oxides, transition metals, and transition metal dichalcogenides, is essential for effective study. This review aims to explore the transport models that elucidate the conduction mechanisms, various synthesis methods, and key physical properties, including electrical, optical, and mechanical attributes. Additionally, recent advancements in their applications, such as energy storage, photocatalysis, anti-corrosion coatings, biomedical uses, and sensing technologies, are discussed. The structural properties of these composites significantly influence their performance. The electrical properties of polymers are often associated with dielectric behavior and electrical conductivity. While most pristine polymers act as insulators due to their covalent nature and lack of ionic or electronic pathways, conducting polymers are exceptions. The incorporation of various conductive nanomaterials into the polymer matrix can enhance its conductivity and overall performance [1].

The integration of conductive matrices into polymers introduces fascinating electrical properties. For instance, incorporating graphene sheets can create interconnected pathways for electron transfer within the nanocomposite, significantly enhancing its electrical conductivity. Today, materials like copper and aluminum dominate as preferred conductors due to their low resistivity, excellent mechanical strength, corrosion resistance, ductility, and other advantageous properties. The demand for materials with low resistivity has grown substantially compared to the past. Superconductors, however, occupy a unique category. While virtually any material can exhibit superconductivity at extremely low temperatures, there are no universal rules to predict whether a material will become superconducting or at what temperature this transition will occur. When we observe the world around us, it becomes evident that the production or extraction of pure metals is a complex, time-consuming, and costly process. From a young age, people are taught to avoid touching frayed electrical cords to prevent electric shocks from exposed conductive wires. Plastics, known for their insulating properties, are commonly used to coat electrical wires, safeguarding users from electric currents. Polymers (plastics) are often viewed as lightweight alternatives to heavier materials like steel and wood, and they are traditionally employed as insulators to prevent electric shocks from live conductors. The discovery that certain polymers, typically associated with insulation, could conduct electricity as efficiently as metallic copper was groundbreaking and unexpected. This revelation, which earned the 2000 Nobel Prize in Chemistry, challenged conventional understanding and opened new possibilities for the use of conductive polymers in various applications [1].

In 2000, the Nobel Prize in Chemistry was awarded to three remarkable scientists—Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa—for their groundbreaking work in the field of conductive polymers. Alan J. Heeger, a professor of Physics at the University of California Santa Barbara, has made pioneering contributions to semiconducting and metallic polymers. He also founded UNIAX Corporation in 1990 and was appointed Chief Scientist of the company in 1999 [2, 3]. Alan G. MacDiarmid, a Professor of Chemistry at the University of Pennsylvania, is renowned for discovering the field of conducting polymers, also known as synthetic metals. In 1977, he achieved a significant breakthrough by chemically and electrochemically doping polyacetylene. Their research has had a profound impact on materials science and opened new avenues for technological advancements [3].

2. Materials and Methods

Band Structure for Various Materials:

Polymers are organic macromolecules consisting of long carbon chains formed by repeating units called monomers, which are bonded by covalent bonds. A single monomer serves as the raw material to produce a polymer. Most polymers are insulators due to the lack of free electrons needed for conductivity. In covalent bonds, electrons are tightly bound and cannot drift when an electric field is applied, resulting in poor electrical conductivity [4]. This phenomenon is further explained by the band theory, which states that electron energy levels are grouped into allowed bands with certain energy levels that are forbidden, known as the band gap. Schrödinger’s Equation, applied to the periodic field of a crystal solid, shows that the lowest energy levels, called valence bands, are inactive in electrical conduction, while the highest energy levels, called conduction bands, participate in electrical conduction.

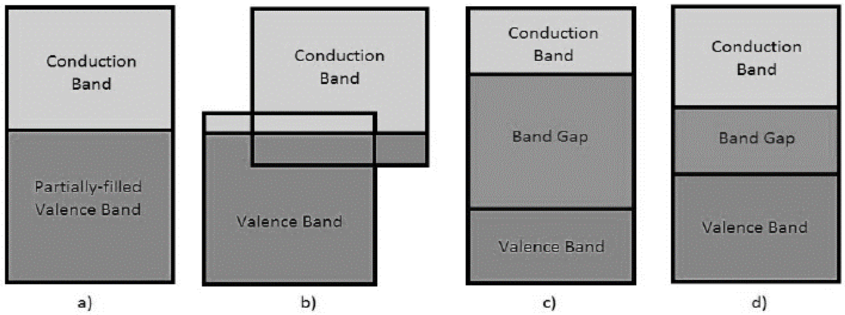

Figure 1. Band Structure for Conductors, Semiconductors, and Insulators: (a) monovalent metals; (b) divalent metal; (c)Insulators; and (d)Semiconductors

Some conductors have a partially filled valence band, making it easier to excite electrons to higher energy levels. In the case of divalent metals, there is an overlap between the empty conductive band and the fully filled valence band. For semiconductors and insulators, valence electrons must cross the band gap to achieve conduction. Semiconductors have a relatively smaller band gap energy compared to insulators. Initially, polymers were considered insulators until 1970, when Shirakawa, Heeger, and MacDiarmid produced the first intrinsic conductive polymer. This breakthrough involved exposing polyacetylene to dopant compounds—either oxidizing or reducing agents, electron donors, or electron acceptors. Their pioneering work ultimately earned them the Nobel Prize in Chemistry in 2000 [4].

Conductive Polymeric Materials:

An electric current arises from the orderly movement of charges in a material when a voltage is applied. Positive charges flow in the direction of the electric field, while negative charges move in the opposite direction. In most materials, electric conduction occurs due to the flow of electrons. Conductive materials have conjugated chains, with alternating single and double bonds between atoms. Doping conductive polymers is easier because of these conjugated bonds, leading to defects and deformations in the polymer chain. These electron-deformation pairs, known as polarons, are responsible for conductivity in polymers. Other quasi-particles, such as bipolarons and solitons, also contribute to the conductivity mechanism [5]. The specific quasi-particle formed depends on the dopant used. The charges resulting from the doping process in conductive polymers enhance their conductivity. The constant movement of double bonds to stabilize charges in neighboring atoms, known as resonance, leads to charge movement and, consequently, conductivity. This movement involves delocalized electrons within a molecule, where an electron in a π bond is shared by three or more atoms. Polaron formation changes the band structure of the conductive polymer, creating polaronic conduction bands within the band gap. This reduces the band gap energy, enabling the polymer to conduct electricity. The conductivity of a conductive polymer is primarily due to the charges formed by the dopant. As the doping level increases, more charges are created in the polymer, leading to greater conductivity.

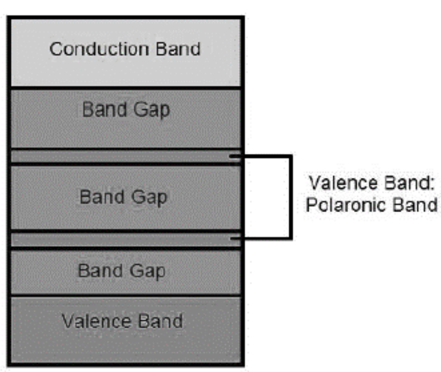

Figure 2. Band Structure of a Conductive Polymer.

Conductivity is also temperature-dependent. As temperature rises, molecules move farther apart, making the doping effect more effective and increasing the doping level and conductivity. Additionally, the relationship between electron energy and temperature, described by the Boltzmann relationship, means that higher temperatures provide electrons with greater energy, making it easier for them to be excited to the conduction band. The most well-known and extensively studied conductive polymers are polyacetylene, polyaniline, and Polypayrrole, thanks to their wide range of applications [5].

Polyacetylene (PA)

Polyacetylene is an organic polymer with the repeating unit C2H2. The polymer consists of a long chain of carbon atoms with alternating single and double bonds between them, each bonded to one hydrogen atom.

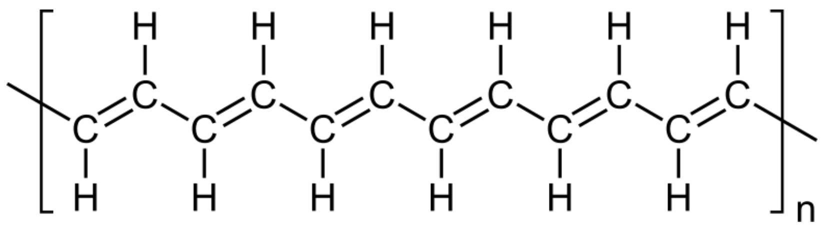

Figure 3. Polyacetylene Polymer Chain structure.

Polyacetylene played a significant role in the research that earned the Chemistry Nobel Prize in 2000. It is synthesized by reacting acetylene (commercially known as ethyne) with a Ziegler-Natta catalyst. Polyacetylene is one of the simplest polymers that exhibits high conductivity. The alternating double and single bonds in its structure allow for resonance, which contributes to its conductive properties. When dopants are added, they introduce charges into the polymer chains. The movement of these charges, facilitated by resonance when an electric field is applied, results in the material's conductivity [6].

Polypyrrole (PPy)

Polypayrrole is one of the conductive polymers that was part of the Nobel Prize-winning research. It is synthesized through the oxidation of pyrrole, resulting in the structure shown below.

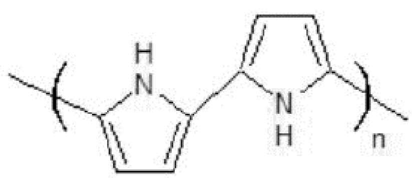

Figure 4. Chemical Structure of the Polypayrrole: Molecule designed on *ChemSketch*.

The redox process involves the addition of an anion to the structure, which is responsible for the conductive properties of Polypayrrole. Similar to other conductive polymers, resonance occurs to stabilize the carbocation, allowing charge movement and resulting in conductivity [6]. This mechanism is similar to that of other polymers studied in the research.

Polyaniline (PANI):

Polyaniline is one of the most promising and extensively studied conductive polymers. It is a family of polymers characterized by aromatic rings connected by nitrogen atoms. Its structure consists of x units of reduced species alternating with 1-x units of oxidized species.

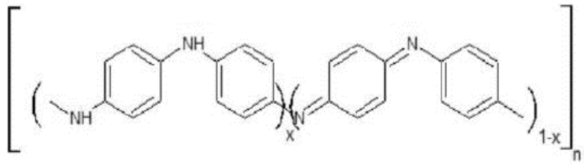

Figure 5. Chemical Structure of the Polyaniline.

The doping process involves protonating the nitrogen atoms in the amine groups of polyanilines with an acidic solution, which oxidizes the structure. This results in the formation of positive charges that move as the structure resonates [7]. As doping continues, charges appear in the structures and are stabilized by resonance, leading to increased conductivity.

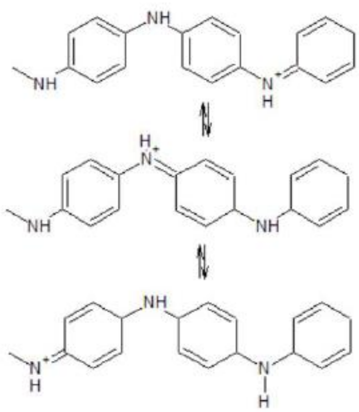

Figure 6. Resonance Mechanism of Polyaniline.

3. Results and Discussion

Synthesis of Conductive Polymers:

There are three main methods to produce conductive polymers: reactional chemistry, electrochemical, and photo-electrochemical, with reactional chemistry being the most commonly used due to its high profitability and efficiency [7].

1. Reactional Chemistry: This chemical process involves the union of monomers by adding oxidizing or reducing agents, converting the neutral polymer into a cationic or anionic complex. The reaction ends with the bonding of this complex to the counter-ion of the redox agent. This process requires high control because it is highly exothermic and emits gases, necessitating proper treatment and protective equipment.

2. Electrochemical Method: This method entails the electronic deposition of the polymer on an electrode. The solution containing the monomers and dopants immerses the electrode. When a sufficiently strong voltage or current is applied, the monomers oxidize, resulting in polymerization. The polymers form in the shape of the electrode and require further processing to achieve the desired shape.

3. Photoelectrochemical Process: This process relies on photoexcitation of the polymer or compounds with catalytic properties in the presence of light, leading to the oxidation of monomers and polymerization. Although this process is simple and environmentally friendly, the resulting polymer's mechanical properties are not as favorable [7, 8].

These methods highlight the diverse approaches to creating conductive polymers, each with its own advantages and challenges.

Properties of Polymeric Materials:

The electrical properties of a material are typically explained using its electronic band structures. The energy difference between the conduction band and the valence band determines whether materials are insulators or conductors. Intrinsically conducting materials have a decreased bandgap, with overlapping conduction and valence bands. While electronic band theory provides a clear explanation for conducting polymers, other studies have also investigated their transport properties. All conducting polymers have conjugated bonds in their backbones, facilitating electron movement. A single bond contains a localized σ bond, while a double bond includes both σ and weaker π bonds. The π bond between the first and second carbons transfers to the second and third carbons, and so on, allowing electrons to flow. Conductivity varies significantly depending on the dopant material, polymer chain arrangement, and length. The dopant concentration and pH value also enhance conductivity. For example, polyaniline exhibits excellent conductivity when the pH is maintained between 0-3, [8].

a. Conductivity:

Conductivity in polyacetylene is the reciprocal of resistance (R^-1), where R is defined by Ohm's Law. Resistance is proportional to the length (l) of the sample and inversely proportional to the cross-section area (A) in Ohmic materials (R = ρl/A), with resistivity (ρ) being the inverse of conductivity [7, 8].

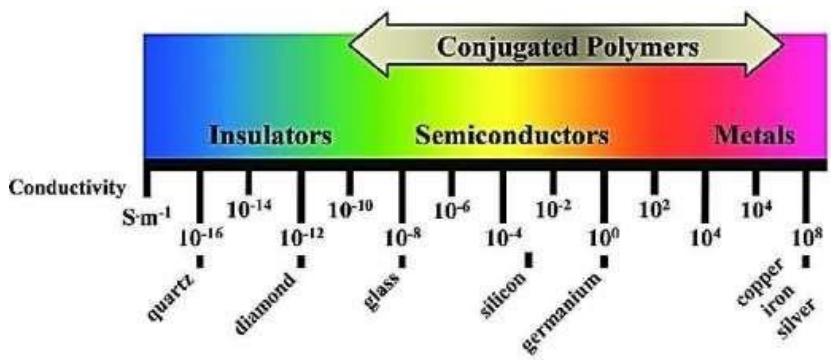

Figure 7. Conductivity: Silver = 1.59 x 10 $^{-8}$, Copper = 1.72 x 10 $^{-8}$, Aluminum = 2.82 x 10 $^{-8}$.

However, semiconductors like polyacetylene typically deviate from Ohm's Law. Conductivity in such materials depends on the number density of charged carriers, their mobility, and temperature. For semiconductors, conductivity generally decreases at lower temperatures. In stretched polymers like polyacetylene, conductivity may be anisotropic, meaning it depends on the direction. Stretched oriented polyacetylene has much higher conductivity in the stretched direction compared to the perpendicular direction. Polyacetylene's alternating single and double bonds create mobile π electrons, which, when doped, result in highly anisotropic metallic conductors [7, 8].

b. Optical Properties:

Conjugated polymers exhibit an anisotropic and quasi-one-dimensional electronic structure due to the presence of π bonds in their backbone, which involve electron–phonon interactions. The electronic transport behavior in organic semiconductors is influenced by charge mobilizers like solitons, polarons, and bipolarons in the ground state degeneracy. Sub-gap optical transitions occur in the polymer backbone, and doping triggers charge mobility by shifting oscillator strength from π to π*. These nonlinear excitations facilitate charge mobility. In their pristine form, conjugated polymers behave like semiconductors, but they exhibit metallic properties when doped with p and n dopants. However, there are conflicts between the nonlinear excitation and photoexcitation of conjugated polymers, such as polarons or bound neutral excitons. To understand the optical properties of conjugated polymers, it is essential to grasp the basic physical properties of simple solids. The optical constants of solids provide a comprehensive understanding of both vibronic and electronic properties when an electromagnetic wave interacts with the polymer [8].

c. **Mechanical Properties:**

The mechanical properties of polymer materials are influenced by monomer arrangement and crystallinity. Crystalline polymers exhibit better mechanical properties compared to amorphous or semi-crystalline polymers. The macroscopic mechanical properties of conducting polymers depend on microscopic changes in the molecular mobility of macromolecules. Factors such as the structure of branching polymer conformations and macroscopic properties like pressure and temperature affect molecular mobility. In amorphous polymers, the monomer distribution and arrangement are random, and crystalline polymers are not stacked. Amorphous polymers exhibit higher molecular motion, and when the temperature reaches the glass transition temperature (T_g), the polymer transforms from a glassy state to a rubbery state, leading to changes in mechanical properties. The mechanical properties of a polymer are also heavily influenced by molecular weight. Parameters such as toughness and strength are related to molecular weight and chain entanglement. [9].

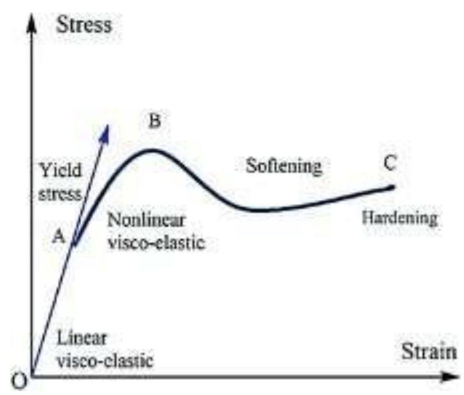

Figure 8 Graph Stress strain.

Defects of Metal Materials:

1. Extraction Process:
   - Copper and other conducting metals are found in high-grade ores.
   - These ores are located in specific places.
   - Mining is costly.
   - Treating large amounts of ore yields only a small amount of metal.
2. Corrosion:
   - Corrosion is a major issue, despite methods like painting and varnishing to prevent it.
   - A significant percentage of metal is lost annually due to corrosion.
   - Corroded metal becomes useless.
   - Approximately 65% of metal is lost per year to corrosion.
3. Other Issues:
   - Low flexibility.
   - High weight.

These defects highlight the challenges associated with the extraction, maintenance, and use of metal materials [9].

Advantage Properties of Polymeric Materials:

Conductive polymers have generated interest in various fields due to their metallic conductivity properties, inertness, and good mechanical properties. Here are some practical applications:

1. Electronics:
   - Conductive polymers are used in batteries, sensors, and microelectronic devices.

- Polypayrrole and polyaniline are used as anti-corrosive coatings for metal protection.

2. Medical Field:

- Conductive polymers are used to produce artificial muscles, biosensors, and drug controlled-release agents.

3. Renewable Energy Resources:

- Scientists are developing eco-friendly, high-energy renewable energy resources, including supercapacitors, fuel cells, and wind energy.

- Supercapacitors are particularly of great commercial interest for future markets like wearable devices and electric vehicles. Unlike conventional capacitors, supercapacitors store 1000 times more energy, have high-speed charge-discharge cycles, and exhibit high energy and power density with good cycle life.

Due to climate change, global warming, and health issues, replacing conventional energy sources with these advanced materials is crucial for addressing social and environmental problems [9].

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Future Prospects and Recommendation:

Conductive polymers offer a wide range of applications, but in some cases, metals remain the preferred option due to their high conductivity and cost-effective processes. However, the unique properties of conductive polymers will be advantageous in certain applications.

1. Weightless Properties: Polymers are lighter than metals, making them ideal for electronics, resulting in smaller and more compact devices.

2. Electromagnetic Interference (EMI) and Radiofrequency (RF) Shielding: Conductive polymers are likely to find acceptance in markets requiring EMI and RF shielding.

3. Biocompatibility: The development of muscles using conductive polymers shows promise, and future research on their biocompatibility will be beneficial.

4. Optimization: Scientists continue to investigate the effects of doping levels, temperature, and band gaps to determine the optimal conditions for achieving the best conductive polymers.

These prospects highlight the potential for conductive polymers to excel in specific applications where their distinct properties offer significant advantages [13].

4. Conclusion

To date, numerous studies have focused on the fabrication of conducting polymers. The primary aim of this review is to explore the current trends in the synthesis, properties, and applications of these materials. Conducting polymers and their composites are notable for their metallic conductivity when doped and their excellent physical properties.

Literature reviews indicate that, in their pristine form, conducting polymers behave as insulators or semiconductors. They only exhibit metallic conductivity when doped with suitable dopants or combined with foreign materials. The physical and chemical properties of conducting polymers depend on their morphology, and different morphologies result in distinguishable properties. Understanding these basic properties is crucial for designing conducting polymers for various applications. The complex structure of conducting polymers and their derivatives poses a challenge for theoretical modeling. Therefore, understanding the origin of conductivity and the doping mechanism is essential. Charge carriers develop on a polymer backbone when added to or extracted from the delocalized π bond. Parameters such as temperature, dopants, and structural properties affect transport properties.

Conducting polymers are widely used as supercapacitor electrode materials due to their metallic conductivity, flexibility, processability, and ease of fabrication. They exhibit high specific capacitance and deliver energy rapidly. However, the main disadvantage of conducting polymer-based supercapacitors is their cycle life; symmetric conducting polymer supercapacitors have a shorter cycle life compared to carbonaceous material-based supercapacitors. Literature suggests that the cycle life problem can be mitigated through irradiation, sonication during synthesis, or compositing with carbonaceous or non-carbonaceous materials. In an asymmetric configuration, using conducting polymers and their derivatives as positive electrodes and carbonaceous materials as negative electrodes can provide higher cycle life and specific capacitance. Stability and cycle life can also be improved by incorporating metal oxides, transition metals, transition metal dichalcogenides, and carbonaceous materials. Future research should focus on developing hybrid conducting polymer composites to achieve better supercapacitor performance. Among conducting polymers, polyaniline and polypyrrole have been effectively used for electrochemical sensing applications. Nanostructures of conducting polymers hold great potential for sensing applications due to their high surface area and high surface-to-volume ratio for the diffusion of analyte gas molecules. The morphology and film thickness of conducting polymers play a crucial role in sensing action by affecting inter-domain spacing and reducing the interaction of analyte gas with the polymer. Polyaniline demonstrates better sensing behavior due to its reversible doping mechanism. Hybrid conducting polymers overcome the drawbacks of selectivity and high working temperatures of metal oxide chemiresistors .Further exploration of polyaniline, Polypayrrole, and their combinations for detecting oxidizing and reducing gases is recommended. Future developments should also focus on other conducting polymers.

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