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A Comprehensive Study of Conductive Polymer Matrix Composites: A Review.

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ABSTRACT

In this paper, we present a summary of some of the theoretical aspects of conductive polymers as well as applications. Additionally, a detailed description of the theories proposed to elucidate the nature of conductivity in conductive polymers. In a similar vein, the paper highlights the theory behind the formation of polaron and bipolaron which represents the most acceptable justification for the conductivity in this class of polymers. Experimental findings have showed what the factors are influencing the conductivity of the conductive polymers which will be discussed with some elaboration.

Keywords: Conducting polymers, Conjugation, energy bands.

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INTRODUCTION

Historical background of the development of conducting polymers

Conventionally, polymers were thought to be as insulators, but in 1970s a discovery by Alan J. Heeger et al. [1-3] changed that idea. Their findings showed that the conductivity of polyacetylene after being doped with an electron-withdrawing AsF₅ significantly increased up to about 10³ S/cm. Several years later, a collection of stable conducting polymers, including polypyrrole (PPy), polyaniline (PAn), and polythiophene (PTh), were reported during the period of 1970s to 1980s, which significantly supported and pushed the research forward on conducting polymers. As a matter of fact, the conductivity of the vast majority of conjugated polymers within the order of 10⁻³–10³ S/cm after doping.

In 1990, Friend et al [4] found that poly(p-phenylene vinylene) (PPV) has an electroluminescent characteristics and established a new field of polymer light-emitting diodes (PLEDs) with semiconducting intrinsic conjugated polymers. In 1995, Heeger et al. [5-6] stated that the bulk-heterojunction polymer solar cells (PSCs) with a conjugated polymer MEH-PPV as donor and a fullerene derivative PCBM as acceptor, which further extended the research on conjugated polymers to the field of organic photovoltaics. Since that time, conjugated polymer optoelectronic materials and devices including PLEDs and PSCs have attracted a lot of attention. Based on the importance of these materials and their outstanding application. Heeger et al [7] were awarded the Nobel Prize in Chemistry in 2000, as an appreciation for their great contributions to the discovery and developments of conducting polymers.

The main advantages of conducting polymers as they possess not only an interesting electronic and optical properties similar to semiconductors, but also the flexible mechanics and process ability. Additionally, there is special electrochemical redox activity with conducting polymers. Obviously, conducting polymers, including doped conducting polymers and intrinsic semiconducting conjugated polymers, play an important role in developing organic optoelectronic and electrochemical devices [8-10].

Applications of conductive polymers

The information presented here in this section will summarize the impact of Heeger et al [1] work on the development of conductive polymers. The main significance of using polymers in general is the affordability using solution-processing of film-forming polymers. Light displays and integrated circuits, for example, could theoretically be manufactured using simple inkjet printer techniques [11-16]. Table 1 explains applications of some conducting polymers. Figures 1-5 explain chemical structure of this conducting polymers.

Table 1: Applications of some conducting polymers

polymer	Application
Doped polyaniline	acts as a conductor and for electromagnetic shielding of electronic circuits. also used as a corrosion inhibitor
Poly(ethylenedioxythiophene) (PEDOT) doped with polystyrenesulfonic acid	used as an antistatic coating material to evade any electrical discharge upon exposure to photographic emulsions and also plays as a hole injecting electrode material in polymer light-emitting devices
Poly (phenylene vinylidene) derivatives	widely exploited for the active layer in pilot production of electroluminescent displays (mobile telephone displays) .
Poly (dialkylfluorene) derivatives	used as the emissive layer in full-colour video matrix displays .
Poly (pyrrole)	has been tested as microwave-absorbing “stealth” (radar-invisible) screen coatings and also as the active thin layer of various sensing devices .

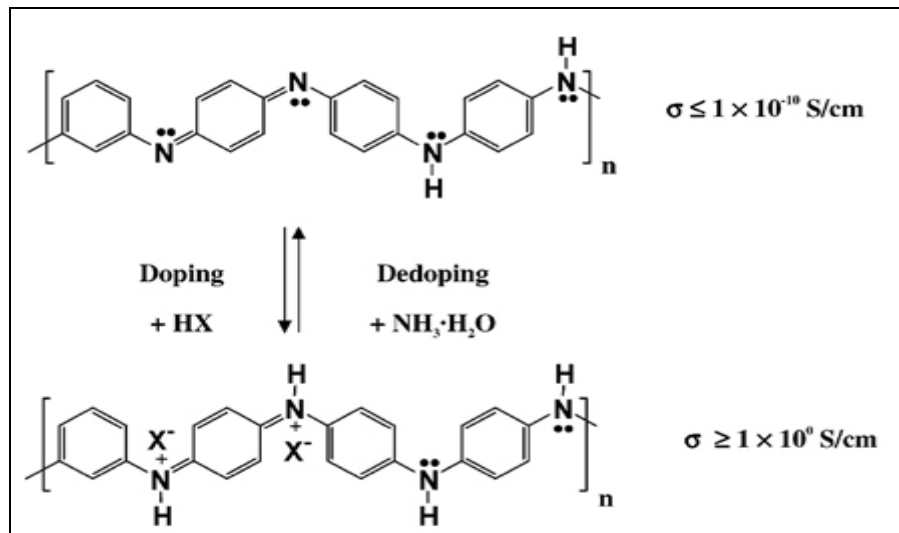


Figure 1: Chemical structure of poly aniline with explain to reversible mechanism of doping.

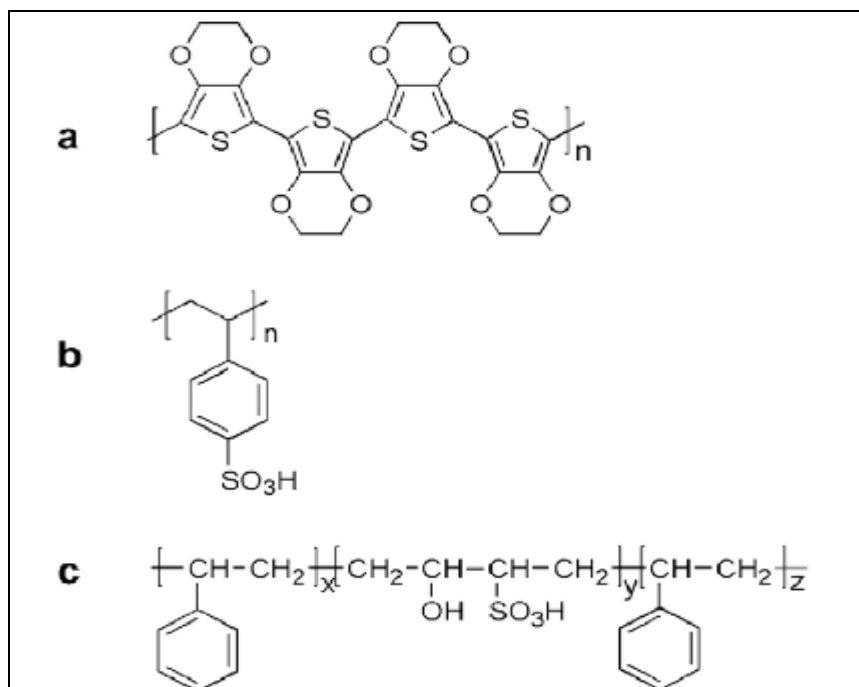


Figure 2: Chemical structures of (a) poly(3,4 ethylenedioxythiophene) (PEDOT), (b) polystyrenesulfonic acid (PSS), and (c) partially sulfonated poly(styrene-b-butadiene-b-styrene) (s-SBS).

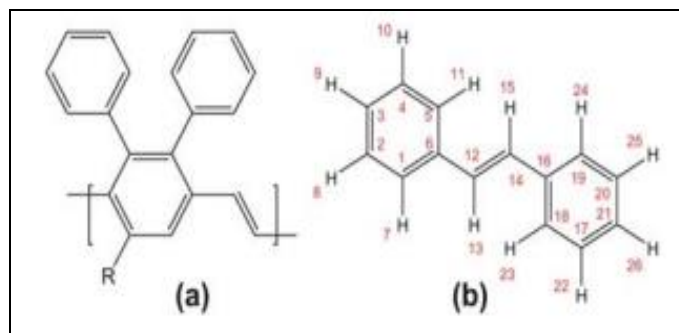


Figure 3: (a) Chemical structure of DP-PPV derivatives. $R \frac{1}{4} C_6H_{13}$ corresponds to DP6-PPV and $R \frac{1}{4} C_{10}H_{21}$ to DP10-PPV. (b) Transstilbene - a monomer of poly-(phenylene vinylene) used to validate the reparametrized atomistic force-field.

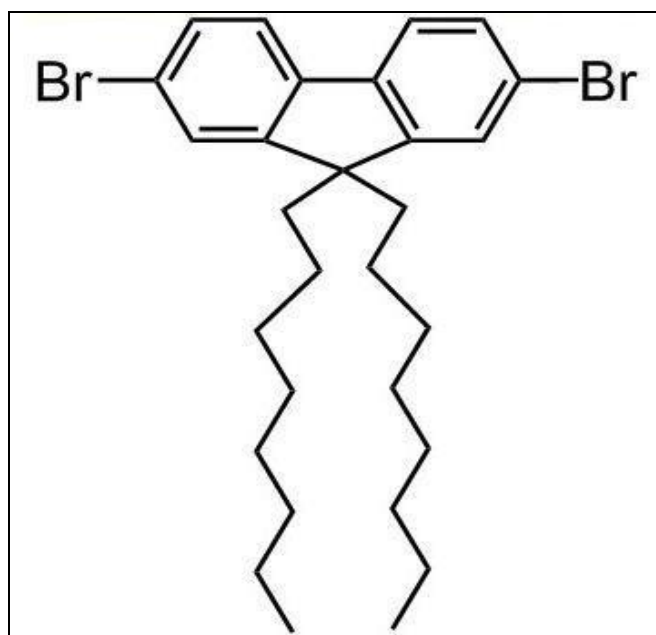


Figure 4: Chemical structures of 9,9-dioctyl-2,7-bibromofluorene.

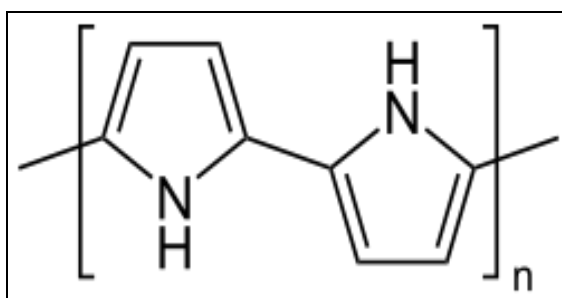


Figure 5: Chemical structures of Poly (pyrrole).

Potential implementation of conductive polymers may include supercapacitors and electrolytic-type capacitors. Some conductive polymers such as polyaniline show a whole range of colors because of their protonation and oxidation forms.

Factors influencing the Conductivity in Conductive Polymers

Factors that affecting the conductivity of conductive polymers are elaborated as follows:

Conjugation length

The presence of conjugation has been a common characteristic among all conducting polymers. It has been found that the conjugation length in polymer chain is important for its electrical conductivity. The conjugation length of a polymer chain is the average distance between two isolations of conjugation. It has been experimentally found that conductivity decreases rapidly with decreasing conjugation length.

Temperature

Effect of temperature on conductivity can be well understood by defining two conductivity systems:

- The high conductivity system with conductivity $>1000 \text{ S cm}^{-1}$, and
- The moderate and low conductivity system with conductivity $<100 \text{ S cm}^{-1}$.

Conductivity of polymers basically is proportional to temperature. This temperature dependence of conductivity varies according to two factors:

Type of Conductivity System:

- Medium & low conductivity systems: Conductivity disappears as $T \rightarrow 0$.
- High conductivity systems: Conductivity remains fixed

Level of Doping:

- Low Doped Sample: Temperature dependence of conductivity is very drastic.
- High Doped Sample: Conductivity is nearly temperature independent.

Doping level

The conductivity of conjugated polymers is found to be increased with increasing the doping level of polymers. The doping level of polymer is determined by the dopant concentration expressed in mol %.

Frequency Dependence

The electrical conductivity of conducting polymers can be decomposed into a DC part and an AC contribution. The DC contribution is frequency independent because in this case, current path involves several long distance hops resulting in low DC conductivity. The AC contribution, on the other hand, increases linearly with frequency because electric field reverses sign while electron is waiting to hop [17].

Mechanism of electrical conduction in conducting Polymers

The conduction properties of conducting polymers have previously been elucidated on the basis of the band theory of solids. According to this theory of solids, when a large number of atoms or molecules are brought together to form a polymeric chain or a crystalline solid, an energy band is formed through the interaction of the constituent atomic or molecular orbitals. The band of highest energy that is completely filled by electrons is generally called the valance band. The electrons associated with bands are involved in chemical bonding and are consequently rather localized and are not free to move through the solid. The lowest lying unoccupied levels form a band which is generally called the conduction band. There is a forbidden energy region between the valance band and the conduction band. This energy separation is called the energy gap or band gap. e.g. when the energy gap is large the material behaves as an insulator. Organic polymers are generally insulators because of their quite wide band gaps. Consequently, there are no charge carriers to support conduction. The appropriate charge carriers may be generated in an organic polymer by its partial oxidation or partial reduction with appropriate dopants. The tendency of an organic polymer to be oxidized or reduced is determined by its electronic properties such as the lowest ionization potential and highest electron affinity. Once charge carriers are generated in this way, the system becomes conducting and the effective mobility of these carriers is determined by the corresponding band width. In other words, the conduction properties of organic polymers are related to their electronic properties such as band gap, ionization potential, electron affinity and band width. See Figure 1 which shows the valence and conduction bands (energy levels) and the band gap for polymers as insulator.

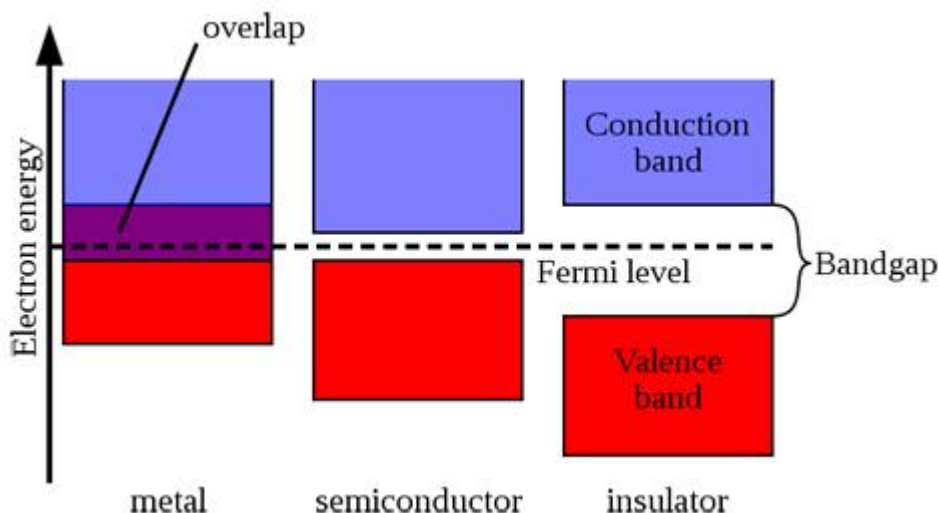


Figure 6: The valence and conduction bands (energy levels in this case) and the band gap for polymers as insulator.

It was supposed that upon doping, the oxidant removed electrons from the filled valence band and reductants added electrons in to the vacant conduction band. However, this model was not useful to compile the conduction mechanism in polyacetylene and other conducting polymers, because from experiments, it was found that the conduction is due to the charge carriers that do not have free spins [18]. To interpret the conduction mechanism in conducting polymers, a new concept called “soliton” was introduced by A.J. Heeger and et al. in 1980 [18]. In this concept, charged solitons are believed to be the conducting species and responsible for charge transport. Charged solitons are a type of charge defects introduced in a polymer chain on doping with electron acceptors or electron donors. This model was initially appealing because charged solitons have no spin and the conducting polymers are found to possess spinless transport. The conducting mechanism of polyacetylene agreed with soliton theory because polyacetylene has a degenerate ground state (i.e., two geometric structures corresponding to the same energy). But all other conductive polymers have non-degenerate ground state.

The soliton concept has not led to grasp the main reason for the origin of conductivity in conductive polymers. That is why a new concepts called polaron and bipolaron have been introduced [19]. According to these concepts, the polymer chain is ionized on doping and this ionization process yields polaron (radical ion) on the chain. At low doping level this polarons are the carriers of electricity. On increasing the doping level the concentration of polaron increases and this results in a probability of interaction with each other, which can be either attractive or repulsive. As a result of this attraction, two polarons may get coupled to form a bipolaron. Bipolarons are doubly charged but spinless. A bipolaron is thermodynamically more stable than two polarons. In the case of polyacetylene, it is believed that due to the degenerate ground state, the bipolarons initially formed disintegrate into polarons which further decay into spinless charged solitons. Among the conjugated organic polymers, polyacetylene represents a special case because it has a degenerate ground-state, and therefore the conduction in it is due to soliton and not due to polarons and bipolarons.

The practical realization and the competitiveness of the innumerable applications based on conductivity depend on the stability of the conducting polymers under environmental conditions. Under ambient conditions polyacetylene loses its conductivity during 30 days by a factor of 1000 [20], while for polypyrrole a conductivity decrease of only a few per cent is observed over 200 days. A loss of conductivity as found for polyacetylene is intolerable for practical uses. The stability of polypyrrole is comparatively better and may be sufficient for applications which do not demand the conductivity to remain exactly constant. The effectiveness of antistatic devices and shielding equipments for electromagnetic interference, for example, are only weakly influenced by small changes in conductivity [21].

CONCLUSION

In the light of the present review, the nature and properties of conductive polymers were discussed with reasonable elaboration. Additionally, the effect of temperature, conjugation length, doping, and frequency were

elucidated. The conductive polymers as a class of polymers have attracted a lot of attention and used in various application based on their electronic properties which were presented in this review.

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