



Comparative Study of Electrical Conductivity in Iodine-Doped Polymer Thin Films

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Abstract— This paper presents a comparative analysis of the electrical conductivity of iodine-doped polymer thin films prepared using different polymer materials and doping concentrations. Polymer thin films have gained significant attention due to their lightweight nature, flexibility, low cost, and potential applications in electronic and optoelectronic devices. In this work, iodine doping is employed to enhance the electrical properties of the polymer films by increasing charge carrier concentration and improving charge transport mechanisms. The thin films are fabricated using suitable deposition techniques and characterized for their structural and electrical behaviour. A comparison is made between undoped and iodine-doped films to evaluate the influence of iodine incorporation on conductivity. The results indicate that iodine doping significantly increases the electrical conductivity of polymer thin films, although the extent of enhancement varies depending on the polymer type, film thickness, and doping level. The paper highlights the relationship between material composition and conductive performance, providing valuable insights for the development of efficient polymer-based conductive materials for sensors, flexible electronics, and energy-related applications.

Keywords— Polymer thin films, iodine doping, electrical conductivity, charge transfer complex, thin film electronics, conductive polymers.

I. INTRODUCTION

Polymer thin films have gained significant attention in recent years due to their wide range of applications in electronics, sensors, optoelectronic devices, and energy storage systems. These materials are lightweight, flexible, cost-effective, and easy to fabricate, making them suitable alternatives to conventional inorganic materials. However, most pure polymers are electrically insulating in nature, which limits their direct use in conductive applications. To overcome this limitation, various doping techniques are employed to enhance their electrical conductivity.

Among different dopants, iodine is one of the most commonly used and effective dopants for polymer materials. Iodine doping introduces charge carriers into the polymer matrix, which significantly improves the electrical conductivity by facilitating charge transport through the film. The interaction between iodine molecules and polymer chains leads to the formation of charge-transfer complexes, thereby modifying the structural and electrical properties of the thin films. The extent of conductivity enhancement depends on several factors such as the type of polymer, film thickness, doping concentration, and preparation method.

This comparative study focuses on the electrical conductivity behavior of iodine-doped polymer thin films

prepared from different polymer systems. The main objective is to analyze and compare the conductivity changes before and after iodine doping and to understand how different polymers respond to the doping process. Such studies are important for selecting suitable polymer materials for advanced electronic and functional device applications. The findings of this work contribute to the development of efficient conducting polymer-based thin films with improved performance and broader technological relevance.

A. Mechanism of Conductivity Enhancement by Iodine Doping

The enhancement of conductivity in iodine-doped polymer thin films is mainly attributed to the **charge-transfer interaction** between iodine molecules and the polymer backbone. When iodine is introduced into the polymer matrix, it can accept electrons from electron-rich sites or conjugated segments in the polymer chain. As a result:

- Positive charge carriers (holes/polarons) are created in the polymer backbone.
- Iodine species such as I_3^- or I_5^- may form within the matrix.
- The effective **band gap decreases**, improving carrier transport.

- The density of localized states in the gap increases, facilitating hopping conduction.

For plasma-polymerized polyterpenol films, iodine exposure reduced the optical band gap to about **1.5 eV** and simultaneously increased conductivity by over an order of magnitude, supporting the charge-transfer mechanism.

II. LITERATURE REVIEW

A.I. Barzic et.al. (2019) - This work deals with the effect of chemical structure and iodine doping on electro-optical characteristics of different polysilanes in the solid state. The properties of polymethylphenylsilane homopolymer were compared with those of polysilane copolymers containing diphenylsilylene structural units associated with either methylhydrogen- or methylphenylsilylene moieties. Their optical parameters, such as Urbach energy and optical band gap, were evaluated using the method proposed by Tauc. The forbidden gap values for the studied polysilanes are reduced after doping from 3.22-3.46 eV to 2.47-2.64 eV, while the electrical conductivities were found in the range of 6.2×10^{-11} - 1.2×10^{-8} S/cm for pristine samples, and increased by 2-3 orders of magnitude following their doping, depending on the nature/content of the organic substituents attached to the silicon main chain. A simple mathematical approach starting from Tauc classical theory was used to establish allowed direct optical transitions for both undoped and doped polysilane samples. The obtained data indicated that the polysilane films with a high content of phenyl side groups presented the best properties for their use in electro-optical application [01].

K. Priya Madhuri et.al (2018) - Doping with halide ions is a popular method to alter the properties of metal phthalocyanines (MPcs), particularly magnetic and electrical nature of organic semiconductors for applications in spintronic or electronic devices. Doping can cause a structural rearrangement in MPC packing and the physical properties may be correlated with molecular packing. Films of a planar and magnetic MPC, manganese(II) phthalocyanine (MnPc) is chosen for iodine doping study. The optical, magnetic and the electrical properties of pristine and iodine doped MnPc thin films are investigated and can be directly associated with their molecular structure. 2D grazing incidence Synchrotron X-ray diffraction reveals structural disorder in MnPc films upon iodine infusion induced by the reorientation of ordered, edge-on molecular configuration to tilted and face-on configurations in a random fashion. The film morphology changes accordingly, where in the uniform crystallites reorganize in a disordered manner. The ferromagnetic nature of the pristine film gets weakened due to iodine species and favors antiferromagnetic coupling. The study of electrical properties at room temperature by conducting atomic force microscopy reveals that the conductance is enhanced independently of the film thickness due to disorder induced by iodine inclusion [02].

Hernández-Tenorio et.al (2018) - To obtain heterocyclic polymer thin films, PPy can be synthesized electrochemically and doped with I₂ by a luminescent

discharge plasma in aqueous solution. The film stays as compact layers, and contains micro-granular structure formed by the agglomeration of small spheres whose mean diameter is between 1.27 μm and 4.96 μm , provided that film thickness and spheres diameter increase with time doping. PPy specters showed a very different structure from the common PPy structure. The difference is that the absorption band related with the N-H bonds does not appear. However the absorption showed in 900 cm^{-1} related with =C-H bonds could suggest an overoxidation of the PPy chains. The electrical volumetric conductivity values of PPy and PPy / I film at room temperature (20 °C) are in the range from 1.08×10^{-5} to 6.5×10^{-3} S cm^{-1} , the experimental measurements show that the conductivity increases with the increase in temperature, and activation energy from 0.052 to 1.77 eV; however, E_a is located in the interval of organic semiconductors [03].

Kateryna Bazaka et.al (2017) - Owing to their amorphous, highly cross-linked nature, most plasma polymers display dielectric properties. This study investigates iodine doping as the means to tune optoelectronic properties of plasma polymer derived from a low-cost, renewable resource, i.e., Melaleuca alternifolia oil. In situ exposure of polyterpenol to vapors of electron-accepting dopant reduced the optical band gap to 1.5 eV and increased the conductivity from 5.05×10^{-8} S/cm to 1.20×10^{-6} S/cm. The increased conductivity may, in part, be attributed to the formation of charge-transfer complexes between the polymer chain and halogen, which act as a cation and anion, respectively. Higher levels of doping notably increased the refractive index, from 1.54 to 1.70 (at 500 nm), and significantly reduced the transparency of films [04].

Nunticha Limchoowong (2016)-This method was successfully applied to enrich tomatoes with iodide using a CT-I coating as an edible film. Additionally, the value-added film is ready-to-eat and serves to provide valuable nutrients. These results will soon be used to improve the estimated dietary iodine intake of inhabitants of Thailand, which has a role in reducing the risk of differentiated thyroid cancer. The iodine-doped chitosan coating can extend the shelf life of tomatoes without any changes in the antioxidant activity. Therefore, the CT-I thin film can be used extensively for other types of fruits and vegetables [05].

Lina Fan et.al (2015) - Iodine-doping is used to develop the high-conductivity carbon nanotube (CNT) -polymer composites. We prepared three kinds of CNT-polymer composites by in-suit polymerization, and obtained iodine-doped samples by mechanical mixing. A series of research about electrical conductivity proves iodine doping is an effective way to get high-conductivity composites with heteroatom in the polymer matrix. The conductivity could increase up to 4 orders of magnitude compared to the undoped samples. Based on Hall-effect, Raman and XPS spectra, we propose the synergistic effect between CNT and iodine results in the superior property. When the heteroatom is N, the synergistic effect of iodine and CNT

helps to form stronger p-π conjugate system. The N cation radical (as a kind of carriers) increase with the enhanced conjugate, resulting in the improved conductivity. When the heteroatom is S, CNT and iodine form π-π conjugate system and charge-transfer complex with S separately. The combination of the two interaction induced the boost of the carrier concentration, as well as the conductivity [06].

Table – 1 Compression of Previous Method

Author(s) & Year	Material / Thin Film Studied	Doping / Method Used	Relevance to Present Work
A.I. Barzic et al. (2019)	Polysilane thin films (polymethylphenylsilane homopolymer and polysilane copolymers)	Iodine doping in solid-state polymer films	Demonstrates that iodine doping significantly enhances conductivity and reduces band gap in polymer thin films, directly supporting the present study on conductivity improvement in iodine-doped polymer films.
K. Priya Madhuri et al. (2018)	Manganese(II) phthalocyanine (MnPc) thin films	Iodine doping / halide ion infusion	Highlights that iodine doping not only improves conductivity but also alters molecular packing and electrical pathways, useful for understanding structure-property correlation in doped films.
C. Hernández - Tenorio et al. (2018)	Polypyrrole (PPy) and PPy/I ₂ heterocyclic polymer thin films	Electrochemical synthesis followed by I ₂ plasma doping in aqueous solution	Strongly relevant because it shows iodine-doped conducting polymer films exhibit improved conductivity and thermal activation, useful for comparative temperature-dependent conductivity studies.
Kateryna Bazaka et al. (2017)	Plasma polymerized polyterpenol thin films (from <i>Melaleuca alternifolia</i> oil)	In situ iodine vapor doping	Shows iodine doping as an effective route for tuning both optical and electrical properties of plasma polymer films, supporting multifunctional thin-film applications.
Nunticha Limchoong (2016)	Iodine-doped chitosan (CT-I) edible thin film coating	Chitosan film doped with iodide for food coating	Although not focused on conductivity, this work indicates broader applicability of iodine-doped polymer films and confirms stable incorporation of iodine into biopolymer matrices.
Lina Fan et al. (2015)	Iodine-doped CNT-polymer composites	In-situ polymerization + mechanical iodine doping	Very relevant for explaining charge-transfer mechanisms and carrier enhancement due to iodine doping, which can be used to justify conductivity rise in polymer-based composite thin films.

III. PREPARATION METHODS OF IODINE-DOPED POLYMER THIN FILMS

Iodine-doped polymer thin films can be prepared using several methods:

Solution Casting / Spin Coating

- Polymer is dissolved in a suitable solvent.
- Film is deposited on substrate by spin coating or casting.
- Iodine is added either in solution or by post-exposure to iodine vapor.

Electrospinning

- Used for nanofibrous thin films such as PMMA.
- Iodine can be incorporated directly in the polymer solution.
- Produces high surface area structures that improve dopant diffusion.

Plasma Polymerization

- Monomer vapor is polymerized directly on the substrate.
- Thin films are later exposed to iodine vapor (in situ or post-deposition).
- Enables uniform, pinhole-free coatings with tunable thickness.

Thermal Evaporation / Vacuum Deposition + Post Doping

- Particularly used for semi-conductive thin films such as poly(N-vinylcarbazole)-based films.
- Literature indicates that **post-deposition iodine doping** is superior to ante-doped film formation because heating ante-doped powders may cause degradation and pinhole formation.

IV. COMPARATIVE ANALYSIS OF REPORTED POLYMER THIN FILMS

Table-2 Comparative performance of iodine-doped polymer thin films

Polymer Thin Film	Doping Type / Condition	Key Performance Parameters	Pristine Film Performance	Iodine-Doped Film Performance	Comparative Observation
Polyterpenol Thin Film	Iodine vapor doping (low & high levels)	Electrical conductivity	5.05 × 10 ⁻⁸ S/cm	1.20 × 10 ⁻⁶ S/cm	Conductivity increased by ~24 times, indicating improved charge transport due to charge-transfer complex formation
Polyterpenol Thin Film	Iodine vapor doping	Optical band gap	3.33 eV	2.51 eV (low doping) / 2.29 eV (high doping)	Band gap decreased notably, showing easier electronic excitation and improved

					semiconducting behavior
Polyterpenol Thin Film	Iodine vapor doping	Direct transition energy	3.44 eV	2.93 eV / 2.61 eV	Significant reduction in direct transition energy after doping
Polyterpenol Thin Film	Iodine vapor doping	Indirect transition energy	2.81 eV	1.85 eV / 1.64 eV	Large decrease in indirect transition energy
Polyterpenol Thin Film	Iodine vapor doping	Refractive index (500 nm)	1.54	1.70	Refractive index increased after doping
Polyterpenol Thin Film	Iodine doping + annealing at 100°C (5 h)	Optical stability / band gap recovery	—	Indirect gap increased 1.64 → 1.74 eV after annealing	Slight recovery due to partial iodine desorption, but doped state remained largely stable
P3HT Thin Film	Iodine doping in solution (1–10 mol%)	Optical absorption / structural ordering	Moderate absorption	Enhanced absorption and altered exciton bandwidth	Iodine improved optical response and modified conjugation length
P3HT:PCBM Blend Thin Film	Iodine doping in solution (1–10 mol%)	Photovoltaic efficiency (PCE)	Lower baseline PCE	Improved PCE after iodine doping	Doping improved charge separation/transport in BHJ solar-cell films
Polyaniline (PANI) Thin Film	In-situ iodine doping during plasma polymerization	Electrical conductivity	Low / less conductive	Strongly increased conductivity	Iodine acted as an effective p-type dopant, creating charge carriers
Polypyrrole (PPy) Thin Film	In-situ heated iodine doping	Electrical conductivity	Lower conductivity	Improved conductivity and nanostructure quality	Doping enhanced carrier density and transport pathways

V. EFFECT OF IODINE DOPING ON ELECTRICAL CONDUCTIVITY

A. Influence of Doping Concentration

Conductivity generally increases with iodine concentration up to an optimum level. At low doping levels, the number of charge carriers is insufficient. As doping increases:

- Carrier concentration rises
- Hopping pathways improve
- Resistance decreases

However, excessive doping may lead to:

- Structural disorder

- Dopant aggregation
- Reduced transparency
- Instability due to iodine desorption

In the PMMA study, increasing iodine concentration up to **0.9 wt.%** enhanced conductivity and reduced activation energy, indicating easier charge transport.

B. Influence of Film Morphology

Thin film morphology plays a crucial role:

- Smooth, defect-free films provide continuous conduction pathways.
- Nanofibrous films from electrospinning increase surface area for dopant absorption.
- Pinholes or voids reduce effective conductivity.

The study on organic/inorganic polymer films reported that ante-doped evaporation can produce pinholes due to decomposition-related volatile byproducts, which harms conductivity. Post-doping reduces these defects.

VI. Conclusion

This comparative paper demonstrates that iodine doping significantly enhances the electrical conductivity of polymer thin films through charge-transfer interactions, band gap reduction, and increased carrier density. Among the reviewed systems, plasma-polymerized polyterpenol showed one of the strongest improvements, while PMMA exhibited moderate conductivity enhancement due to its insulating nature. The literature also confirms that post-deposition iodine doping is generally more effective than ante-doped film formation because it minimizes structural damage and improves film uniformity.

In conclusion, iodine-doped polymer thin films are promising candidates for next-generation flexible and low-cost electronic materials. Future work should focus on improving dopant stability, optimizing doping uniformity, preserving transparency, and developing encapsulation strategies to maintain long-term conductivity.

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