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Effect of Iodine Doping on the Conductivity of Polymer Thin Films

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***Abstract*— Polymer thin films have attracted considerable attention due to their lightweight nature, flexibility, low-cost fabrication, and potential applications in electronic and optoelectronic devices. However, most pristine polymers exhibit poor electrical conductivity because of their insulating nature. Doping with electron acceptors such as iodine is a widely used technique to enhance the electrical conductivity of polymer thin films. This paper presents a comprehensive study on the effect of iodine doping on the conductivity of polymer thin films. The mechanism of charge transfer, preparation methods, changes in structural, optical, and electrical properties, and influencing parameters such as doping concentration, exposure time, and film thickness are discussed. Experimental observations from earlier studies indicate that iodine doping significantly increases conductivity by generating charge carriers through oxidation and partial charge transfer interactions. The paper also reviews the applications of iodine-doped polymer thin films in sensors, antistatic coatings, photovoltaic devices, and flexible electronics.**

Keywords*— *Polymer thin films, iodine doping, electrical conductivity, charge transfer complex, organic semiconductors, thin film electronics.

I. INTRODUCTION

Polymer thin films are widely used in modern material science and electronics because of their unique combination of mechanical flexibility, chemical stability, ease of processing, and low production cost. These materials have found applications in organic solar cells, light-emitting diodes, field-effect transistors, sensors, and antistatic coatings. Despite these advantages, a major limitation of many polymeric materials is their inherently low electrical conductivity.

The conductivity of polymers can be improved significantly by introducing dopants. Among the different doping agents, **iodine (I_2)** is one of the most effective and commonly used p-type dopants. Iodine doping enhances conductivity by accepting electrons from the polymer backbone, thereby creating positive charge carriers such as polarons and bipolarons. This charge transfer process transforms insulating or semiconducting polymers into materials with improved electrical transport properties.

Polymer Thin Films

Polymer thin films are thin layers of polymeric material with thickness ranging from a few nanometers to several micrometers. These films may be prepared by techniques such as:

- Spin coating
- Dip coating
- Doctor blade coating
- Drop casting
- Vacuum evaporation
- Electrochemical polymerization

Common polymers used for conductivity studies include:

- Polyaniline (PANI)
- Polypyrrole (PPy)
- Polyacetylene (PA)
- Polythiophene (PTh)
- Polyvinyl alcohol (PVA) composites
- Polysilanes
- Poly(methyl methacrylate) (PMMA)-based blends

B. Advantages of Iodine Doping

- Simple and low-cost process
- Can be performed at room temperature
- Significant conductivity enhancement
- Suitable for a wide range of polymers
- Vapor phase doping provides uniform surface interaction
- No need for complex instrumentation

II. LITERATURE REVIEW

A. Bouzidi et.al (2019) - Undoped PVA and Zinc iodide (ZnI_2) inorganic salt doped PVA with different ZnI2 (1–37) wt% percentages are novel composite polymer dielectric films have been successfully prepared by the solution cast method. The developed dielectric films were characterized by analyzing the physicochemical phenomenon to study the effect of ZnI2 inorganic salt concentrations. The XRD histogram explicated the being semi-crystalline nature of PVA polymeric matrix with ZnI2 inorganic salt doping. The optical UV–Vis–NIR characteristics of the composite dielectric films were measured. The effect of ZnI2 inorganic salt loading contents increasing on opto-electrical properties such as transmittance, Absorbance, optical band gap in addition to the AC impedance spectroscopy was studied in the polymer composite dielectric film. The modifications in the optical properties of PVA film are attributed to the interaction between the salt molecules and the PVA matrix. The frequency dependent AC\DC electric conductivity at different ZnI2 content follows and obeyed the Jonscher's universal power law. The data of AC impedance spectroscopy is to map ready the complex generalization of resistance that includes capacitive and inductive effects of the polymer composite dielectrics as a function of the angular frequency. These films with excellent optoelectronic phenomenon beside appreciable flexibilities aid their claims as multifunctional UV shielding devices with enhanced a character of semiconductors[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].

Teresa Hernández de la Cruz et.al (2018) - The chemical structure, morphology, electromagnetic absorption and electric conductivity of thin films. The electrochemical synthesis of polypyrrole/surfactant (PPy/SDS) films doped with iodine is carried out by glow discharge plasma in aqueous solution, at different reaction times. The morphology shows agglomerations of particles dispersed in the surface. Infrared spectroscopic analysis shows absorption on the wavenumbers 2915, 2362 and 2082 cm^{-1} corresponding to chemical groups C-H, C=O and R/N=C=S, respectively. The electromagnetic absorption had higher response sensitivity between 340 to 800 nm in the visible region, and the electric conductivity of samples oscillated between 5.0×10^{-6} and 2.0×10^{-5} S/cm. The thickness films significantly increased when doping with iodine, reaching values up to 50 μm [03].

Kateryna Bazaka et.al (2017) - Owing to their amorphous, highly cross-liked 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].

E. Bementa et.al (2017) - Three systems of starch-based crust electrolytes were prepared using various gelatinization times, various weight percentages (wt%) of starch, and various wt% of starch incorporated into potassium iodide. All the samples were subjected to electrochemical impedance spectroscopy, X-ray diffraction spectroscopy, scanning electron microscopy, Fourier transform infrared spectroscopy, and transference number measurements. Electrochemical impedance spectroscopy shows that 1.7 wt% of starch has maximized the room temperature conductivity of the electrolyte to 1.4587×10^{-4} S cm^{-1}. The conductivity was enhanced to 4.5278×10^{-4} S cm^{-1} on the increment of starch's wt% from 1.7 to 3.2. This conductivity was further enhanced to 3.4609×10^{-3} S cm^{-1} on the addition of 0.3 wt% of potassium iodide. The conductivity enhancement was found due to the formation of glucosyl carboxonium ions. The effect of longer heating time in gelatinization is attributed to the formation of glucosyl carboxonium ions. X-ray diffraction spectroscopy affirms the reduction in crystallinity of starch. Scanning electron microscopy analysis shows the porous morphology of starch electrolyte, and addition of potassium iodide shows the morphology of bean nuts like particles seated on the pores [05].

Seongwon Yoon et.al (2016) - The effects of iodine doping on small molecule organic semiconductors. Thin films of semiconducting p-DTS($FBTTh_2$)$_2$ doped with 1–5 wt% iodine were fabricated and their photo-physical, crystallographic, morphological, and electrical properties were systematically analyzed. The doping significantly increased the energetic distance between the highest occupied molecular orbital (HOMO) and Fermi level of p-DTS(FBTTh$_2$)$_2$, typical for p-type doping. In addition, depletion mode transistor measurements showed an increase in the hole concentration with increasing dopant concentration. From grazing incidence X-ray diffraction (GIXD) analyses of iodine-doped p-DTS(FBTTh$_2$)$_2$ films, we observed significant changes in the crystal orientation at the optimal doping ratio of 1 wt%. Atomic force microscopy (AFM) analyses showed morphological changes with respect to dopant concentrations, which were in good agreement with the GIXD results. As a result, accumulation mode transistor measurements demonstrated an increase in the hole mobility by 54% at the optimized doping concentration compared to an undoped device. Furthermore, photoconductive device operation revealed that iodine-doping can induce dramatically enhanced photo-responsivity as high as 2.08 A/W [06].

N.A. El-Ghamaz et.al (2016) - The physical properties of PVC was found to be co-related to the doping technique. The presence of iodide ions increase the optical absorbance and electrical conductivity while decrease the thermal stability of the polymer. A charge transfer complex was formed at high concentration of iodine by physical doing technique. It was noticed that both chemically modified polymer and low content of iodine physically doped polymers show similar behavior in optical absorbance and electrical conductivity. Both of direct and indirect optical transition between valance and conduction bands are found to be possible transitions for PVC and composites I and II. Also, iodination process decreases the fundamental energy gap values to 4.67 eV and 3.6 eV for direct and indirect electronic transitions, respectively. The chemical doping technique by Finkelstein Halogen exchange was found to increase the conductivity by 2 orders. Quantum mechanical tunneling (QMT) conduction mechanism is found to be the dominant mechanism for PVC and composite I, while, the non-overlapping small polarons tunneling (NSPT) is the operating conduction mechanism in composite II. The improvement of optical absorbance and electrical conductivity and the decrease in Eg values could propose the iodinated PVC to be used, for example, as an absorber and/or charge transfer layer in polymer based multilayer solar cells [07].

Authors & Year	Material/ System	Method	Key Characterization	Major Findings	Applications
A. Bouzidi et al. (2019)	PVA + ZnI_2 (1–37 wt%)	Solution casting	XRD, UV–Vis–NIR, AC impedance	Semi-crystalline nature; band gap variation; conductivity follows Jonscher's law; improved optoelectronic properties	UV shielding devices, semiconductor films
K. Priya Madhuri et al. (2018)	MnPc iodine-doped thin films	Thin film deposition	GIXRD, AFM, electrical studies	Structural disorder due to iodine; reduced ferromagnetism; increased conductance independent of thickness	Spintronics, organic electronics
Teresa Hernández de la Cruz et al. (2018)	PPy/SDS iodine-doped films	Plasma electrochemical synthesis	FTIR, conductivity, morphology	Increased thickness (~50 µm); conductivity (10^{-6}–10^{-5} S/cm); strong visible absorption	Electromagnetic absorption devices
Kateryna Bazaka et al. (2017)	Polyterpenol (iodine doped)	Plasma polymerization	Optical, conductivity analysis	Band gap reduced to 1.5 eV; conductivity increased; refractive index increased; reduced transparency	Optoelectronic devices
E. Bementa et al. (2017)	Starch + KI electrolyte	Gelatinization method	EIS, XRD, SEM, FTIR	Conductivity enhanced up to 10^{-3} S/cm; reduced crystallinity; porous morphology	Solid electrolytes
Seongwon Yoon et al. (2016)	p-DTS(FBTTh$_2$)$_2$ + iodine	Thin film fabrication	GIXD, AFM, transistor studies	Increased hole mobility (54%); enhanced photoresponsivity; structural reorientation	Organic transistors, photodetectors
N.A. El-Ghamaz et al. (2016)	PVC iodinated composites	Chemical & physical doping	Optical, electrical studies	Reduced band gap; increased conductivity; QMT & NSPT conduction; charge transfer complex formation	Solar cells, absorber layers

III. MECHANISM OF CONDUCTIVITY ENHANCEMENT BY IODINE DOPING

A. *Charge Transfer Interaction*

Iodine molecules withdraw electrons from the polymer backbone, leading to partial oxidation of the polymer. This creates mobile positive charge carriers (holes), which move along the conjugated chain.

B. Formation of Polarons and Bipolarons

Doping introduces localized charge defects:

- **Polarons**: radical cations associated with local lattice distortion
- **Bipolarons**: doubly charged species formed at higher doping levels

These species facilitate charge transport through the polymer matrix.

C. Increase in Density of States

The dopant modifies the electronic band structure of the polymer by introducing energy levels within the band gap. This reduces the effective band gap and enhances electrical conduction.

D. Interchain Transport Improvement

Iodine molecules can improve interchain coupling by inducing structural rearrangement, which helps charge hopping between neighboring chains.

IV. RESULTS AND DISCUSSION

A. Effect of Doping Time

Conductivity generally increases with increasing iodine exposure time up to an optimum value.

- **Short exposure:** insufficient dopant uptake
- **Optimal exposure:** maximum charge transfer and conductivity
- **Excessive exposure:** saturation, instability, or structural degradation

B. Effect of Doping Concentration

Higher iodine concentration usually leads to increased conductivity initially due to greater carrier generation. However:

Very high doping concentration may cause:

- Structural disorder
- Dopant aggregation
- Increased scattering
- Reduced film stability

C. Effect of Film Thickness

Film thickness influences iodine diffusion and charge transport:

- **Thin films:** faster iodine penetration, uniform doping
- **Thicker films:** incomplete doping in inner layers

Therefore, thinner films often show more uniform conductivity enhancement compared to thick films.

D. Comparative Discussion with Previous Studies

Several researchers have reported the conductivity enhancement of polymer thin films after iodine doping:

- **Polyaniline thin films:** Significant increase in conductivity due to protonation and charge delocalization.
- **Polypyrrole films:** Enhanced carrier density and improved electrochemical response.
- **Polysilane films:** Iodine-induced changes in electro-optical and electrical properties due to interaction with Si–Si backbone.
- **Polyacetylene films:** Classic example where halogen doping leads to dramatic conductivity enhancement.
- **Polymer blend films:** Moderate conductivity increase depending on the amount of conducting phase and iodine uptake.

V. Conclusion

The effect of iodine doping on the conductivity of polymer thin films is profound and technologically significant. Iodine acts as an electron acceptor and forms charge transfer complexes with polymer chains, resulting in the generation of mobile charge carriers such as polarons and bipolarons. This leads to a substantial increase in electrical conductivity, often by several orders of magnitude. The extent of conductivity enhancement depends on multiple factors including polymer type, film thickness, doping concentration, exposure time, morphology, and environmental stability.

Experimental and theoretical studies confirm that iodine doping not only improves electrical conductivity but also modifies optical, structural, and thermal properties of polymer thin films. Although issues such as dopant volatility and long-term instability remain challenges, iodine doping remains one of the simplest and most effective methods for enhancing the performance of polymer thin films in electronic and optoelectronic applications.

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