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STUDY OF ELECTRICAL PROPERTIES OF ELECTROACTIVE POLYPYRROLE FABRICATED WITH FLUORESCEIN DYE AS A DOPANT

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Abstract

The research paper aims to focus on the Electrical properties of PPy to elucidate the impact of Fluorescein; a xanthene dye as a dopant dopant. The synthesis method involves the in situ oxidative chemical polymerization of pyrrole in the presence of ammonium peroxydisulphate as an oxidant. Furthur preparation of PPy/Fluorescein composite is done by mixing fluorescein solutions at different concentrations during polymerization proceeds, and the resulting PPy/Fluorescein composite is thoroughly characterized using SEM analysis. The resulting material is subjected to extensive Electrical characterization using four probe conductivity Bridge. The results successfully elucidate the Electrical conductivity at different temperature, providing insights into the influence of fluorescein on PPy's conducting behavior.

Introduction

Conducting polymers, with their remarkable combination of electrical conductivity, flexibility, and ease of synthesis, have attracted substantial attention for applications across various domains, including sensors, actuators, organic electronics, and energy storage devices.[1] Their adaptability, tunable properties, and ability to undergo reversible redox reactions make them particularly promising for the advancement of cutting-edge technologies with enhanced functionality and versatility.[2,3]

Among these materials, Polypyrrole (PPy) has emerged as a standout conducting polymer, celebrated for its unique electronic characteristics. Derived from the polymerization of pyrrole monomers, PPy exhibits a chain-like structure with alternating single and double bonds along its backbone, forming a conjugated pi-electron system responsible for its electrical conductivity.[4] Synthesized through methods such as chemical oxidative polymerization, electrochemical polymerization, and enzymatic polymerization, PPy is renowned for its capacity for reversible doping and de-doping, a process that significantly influences its conductivity. These properties position PPy as an integral material in diverse fields, including sensors, actuators, organic electronics, and energy storage devices, contributing to advancements in flexible and emerging technologies. Furthermore, its tunability and compatibility with various substrates underscore its role as a versatile material for innovative and multifunctional device development.[5,6]

Polypyrrole distinguishes itself with excellent conductivity and environmental stability. However, ongoing efforts to refine its properties for specific applications have driven researchers to explore new strategies, such as doping.[7,8] Incorporating dopants into conducting polymers not only modifies their electrical characteristics but also enhances thermal stability, rendering them suitable for use in diverse thermal environments. The introduction of fluorescein, a xanthene dye recognized for its unique optical properties, into the PPy matrix is anticipated to add functional diversity while potentially affecting the material's electrical behavior.[9]

Fluorescein, known for its fluorescence and distinctive chemical structure, is an appealing choice as a dopant for altering the thermal and electronic characteristics of polymers. Understanding the interaction between PPy and fluorescein is essential for fine-tuning the composite material's properties to meet the requirements of emerging technologies. This research aims to address this need by systematically studying the thermal behavior of PPy when fluorescein is incorporated, shedding light on the intricate relationship between molecular structure, thermal stability, and the electroactive nature of the resulting composites.[10,11]

The study adopts a systematic methodology to explore the thermal and electrical intricacies of the PPy/Fluorescein composite. Synthesis involves chemical polymerization of pyrrole in the presence of varying fluorescein dye concentrations. Morphological and electrical characterization using techniques like SEM and DC conductivity measurements allows for the assessment of the material's electrical performance at different temperatures, offering valuable insights into fluorescein's influence on PPy's electrical behavior.

Experimental:

All the chemicals required in the present work like monomer pyrrole, oxidizing agent, ammonium peroxydisulphate and dopant Fluorescein are of A. R. Grade. PPy/fluorescein composites were synthesized by simple chemical oxidative polymerization method. The aqueous solution of 0.1 M Ammonium peroxydisulphate was prepared. To this solution 0.00001 M aqueous solution of dopant was added with constant stirring. After a vigorous stirring at 50oC drop by drop 0.1 M solution of monomer pyrrole was added. The reaction was stirred for few hours on magnetic stirrer which gives rise to formation of precipitate of polymer composite. This reaction mixture was allowed to stand for 24 hours in order to complete polymerization process. The resulting product was vacuum filtered. The precipitate was washed with copious amount of triply distilled water. Until the washing was clear. Similarly, 0.0001 M PPy/Fluorescein composite was also synthesized. The polymer composite was dried in desiccators and again dried in an oven at 40-50^{o}C. The Electrical characterization of synthesized composites was carried out by using four probe conductivity Bridge.*(12)*

Result and Discussion:

1. **SEM analysis of PPy Composites:**

The resulting morphologies of the synthesized polypyrrole and PPy/Fluorescein composites from SEM could be seen from Figure.

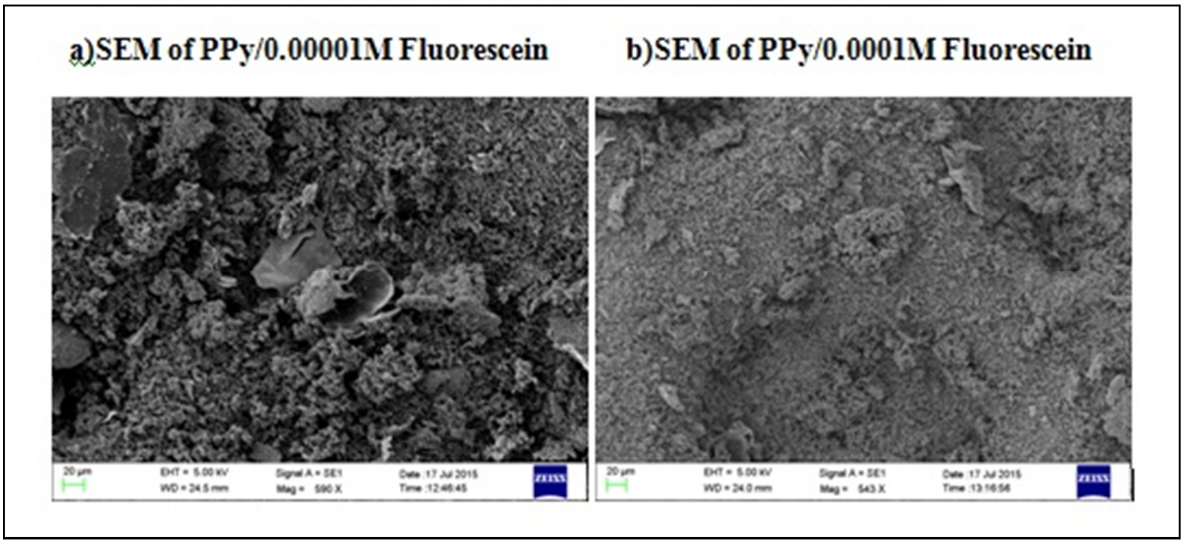

Fig: SEM analysis of PPy/fluorescein dye composites

SEM image of PPy/Fluorescein composite shows irregular polymeric solid structure with rough surface. There is formation of aggregates of polymeric chains is observed.The aggregation of particles which may be due to the increased interchain interaction showing the crystallinity in coincide with the result of conductivity. Thus, the morphology of the conducting polymers is very much related to the electrical conductivity.

PPy structure is more homogeneous than PPy/fluoresceincomposites. The doped films of PPy with Fluorescein dye are having rough, porous surface and having lamellar appearance due to dopant interaction. Uniform, porous and granular surface morphology is shown in each case of the PPY/Fluorescein dye composite samples preferred for applications like gas sensing promoting the adsorption of gas molecules through the surface, though the size of particles effected by pores varies due to the different mole ratios of PPY in each sample.It can be clearly observed that the surface of polymer has been modified into bulky, porous nature and having globular particles which may be due to adsorption of dye at the surface of PPy, when compared to the SEM images of PPy taken before the treatment of dopant.

2. **Electrical Characterization:**

The Dc conductivity of the synthesized PPy and PPy composite materials was measured by four-point probe method at constant current with change in temperature variation of voltage was determined. The Dc conductivity of samples was determined between the temperature range of 35 to 100^0C (308-373^0K) it is observed that the resistance depends upon composition as well as the temperature of the material. The temperature dependence of conductivity for polypyrrole and PPy/fluorescein composites are shown in fig.

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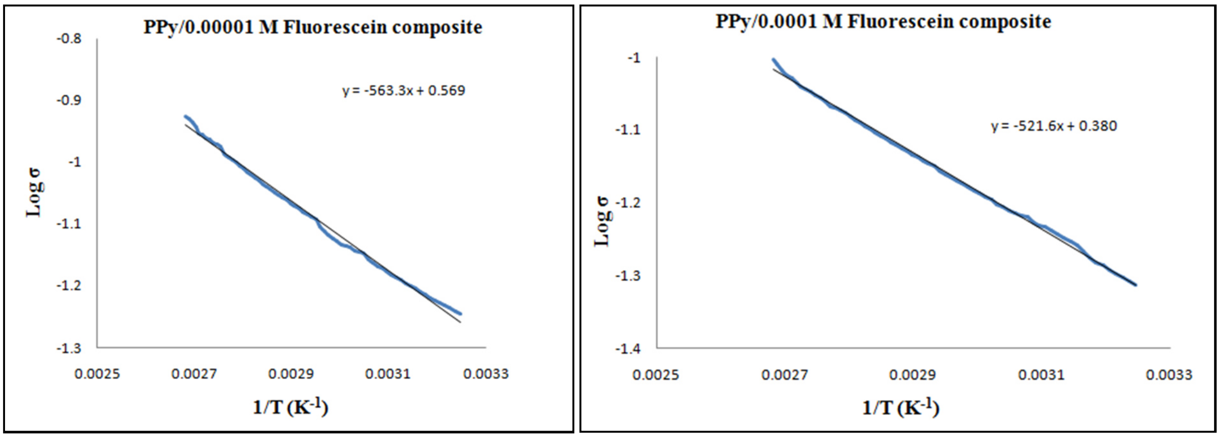

PPy/0.00001 M Flu composite **PPy/0.0001M Flu. composite**

Fig: Variation of Log σ verses 1/T

From these plots it is observed that conductivity increases with increase in temperature. As the temperature increases, mobility of electrons or ions also increases which results into rise in conductivity. The curve is linear. The slope of the curve gives activation energy. The plot shows linear behavior thus this plot is Arrhenius in nature. The value of conductivity suggests that the composite materials synthesized are conductive.

The temperature dependence conductivity for PPy/fluorescein composites is given in the figure-

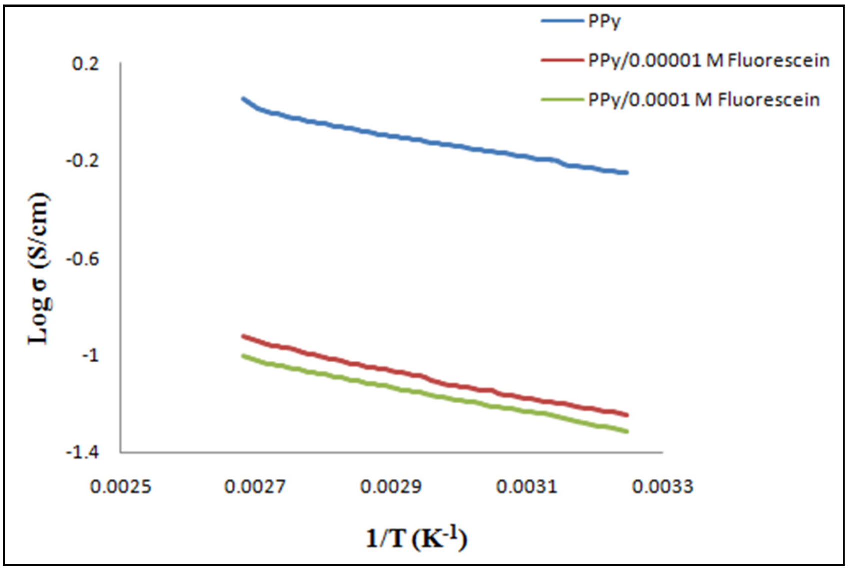

Fig: Temperature dependence conductivity of PPy/fluorescein dye composites

This indicates that conductivity of material decreases with increase in concentration of fluorescein. This is due to the reason that with incorporation of high concentration of dopant molecule in the chain, mobility of electrons is obscured. This may be caused due to majority of short polypyrrole chain lengths that is likely to lead to a higher number of interchain electron transfer events and therefore to a lower conductivity, especially in an amorphous material like the polypyrrole powder synthesized in this work.

Table: Conductivity and activation Energy of PPy/$CeCl_3$ composites

S.N.	Polymer Composite	Conductivity at 341K (S/cm)	Activation Energy (eV)
1.	PPy	0.766504846 7.66x 10^{-1}	6.66816 x 10-21
2.	PPy/0.00001M Fluorescein	0.082331175	7.77354E-21 10 -21
3.	PPy/0.0001M Fluorescein	0.070790633	7.19808E-21

Conclusion:

The surface morphology of the synthesized material was studied by using SEM and XRD spectral analysis which indicates amorphous nature of the synthesized materials with aggregates at some places of the polymer surface. By the SEM image analysis of the obtained films, the influence of dopant inclusions on the morphology of composite films was shown. Electrical characterization by Dc conductivity measurements indicates existence of conducting property in the materials having conductivity in the range 7.079 x 10^{-2} to 7.079 x 10^{-2} and activation energy is also found in the range 7.1980 x 10^{-21} to 7.7735 x 10^{-21}.

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