MORPHOLOGICAL CHARACTERIZATION AND SYNTHESIS OF POLYTHIOPHENE DOPED PVA FILM

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Abstract:- A systematic study of structural and optical properties of “synthesis and characterization of nanomaterial of polythiophene doped PVA film” prepared by solution cast technique. It has been attempted to understand the Structural nature of PVA thin film samples. The morphology of film were carried out by SEM, which report the quite homogeneous and shows no cracks, voids or unevenness. This suggests that after grafting of polyacrylic acid chains onto PVA backbone, the matrix remains homogeneous in composition. XRD technique indicates that the film possesses amorphous nature (i.e.) disorder in polymer chains. These films are suitable for various optical applications, and also in Gas Sensors, Light-emitting diodes(LEDS), micro-valves and actuators. Commercially available applications utilizing conductive polymer also include antistatic coating for electronic packaging and electro chromic windows.

Keywords- FTIR, UV spectroscopy, conducting Polymers (Thin films).

I. INTRODUCTION

Nanotechnology is naturally very broad, comprise the fields of as, surface science, molecular biology, semiconductor physics, micro fabrication etc. Generalized description of Nanotechnology was described by National nanotechnology (US) initiative, defines nanotechnology as at least one dimension sized manipulation from 1 to 100 nm. Synthetic polymers are human-made polymers. From the utility point of view they can be classified into four main categories: thermoplastics, thermosts, elastomers and synthetic fibers. They are found commonly in a variety of consumer products such as money, super glue, etc.

Polyvinyl alcohol (PVOH, PVA, or PVAl) is a water-soluble synthetic polymer (not to be confused with polyvinyl acetate, a popular wood glue). It has the idealized formula [CH₂CH(OH)]ₙ. It is used in papermaking, textiles, and a variety of coatings. It is white (colorless) and odorless. Polyvinyl alcohol has excellent film forming, emulsifying and adhesive properties. It is also resistant to oil, grease and solvents. It has high tensile strength and flexibility, as well as high oxygen and aroma barrier properties. However these properties are dependent on humidity, in other words, with higher humidity more water is absorbed. The water, which acts as a plasticiser, will then reduce its tensile strength, but increase its elongation and tear strength.

PVA has a melting point of 230 °C and 180–190°C (356-374 degrees Fahrenheit) for the fully hydrolysed and partially hydrolysed grades, respectively. It decomposes rapidly above 200 °C as it can undergo pyrolysis at high temperatures. PVA is close to incompressible.

Thiophene, also commonly called thiofuran, is a heterocyclic compound with the formula C₄H₄S. Consisting of a flat five-membered ring, it is aromatic as indicated by its extensive substitution reactions. Related to thiophene are benzothiophene and dibenzothiophene, containing the thiophene ring fused with one and two benzene rings, respectively. Compounds analogous to thiophene include furan
(C₄H₄O) and pyrrole (C₄H₄NH). Thiophene was discovered as a contaminant in benzene. This new heterocyclic compound was thiophene. Polythiophenes become electrically conductive upon partial oxidation, i.e., they become "organic metals. Polythiophene has been widely used in environmentally and thermally stable conjugated polymers, materials, such as chemical and optical sensors, light-emitting diodes and displays, photovoltaic devices, molecular devices, DNA detection, polymer electronic interconnects, solar cells and transistors. Conducting polymer are polymer which have metallic and semiconductor characteristics a combination of properties not shown by any other known material. The presence of conjugated double bonds along the backbone of the polymer is the key property of a conductive polymer. In conjugation double bond, the bonds between the carbon atoms are alternately single and double. The type of conductive polymer which has generated much research activity in the last fifteen to twenty years fits neither intrinsic nor the conductor classification. For example structure of poly-acetylene is shown in figure (1)

![Figure 1: Structure Of Poly-Acetylene](image)

The overall process which is often referred to as classification of conductive polymer.

![Figure 2: Classification of conducting Polymer](image)

**II. MATERIALS AND METHODS**

For preparation of films, for sample-1 is pure PVA and sample-2 (commercially available) Polyvinyl alcohol (HiMedia Laboratories, India) granular; Polythiophene (PT) (HiMedia Laboratories, India); Dimethylformamide (DMF) (HiMedia Laboratories, India); are used. Pure PVA thin film (Sample -1) PVA with molecular weight of 2g/mol (BDH chemicals England) was used as the basic polymeric materials in this work. The PVA solution films with glutaraldehyde (GA) (25% aqueous solution) were
prepared by solution casting method. 1 g of PVA powder was added to doubly distilled water and allowed to swell for 24 h at room temperature. The polymeric solution are continuous stirring in magnetic stirrer. Then the solution was poured into flat glass plate dishes. Homogenous films were obtained after drying in an air oven for 24 h at 60°C. The thickness of the films were in the range of 20 ± 0.05 μm. Images(4) shows the image of films. Synthesis facility is utilised in Nanotechnology lab Gyan Ganga College of Technology, Jabalpur, M.P, INDIA.

Figure 3: Stirring of solution on Magnetic Stirrer

Figure 4: Thin films of Pure PVA (sample -1)

**Polythiophene doped PVA thin film (sample -2)**
Synthesis of PTh :- Two milliliter of thiophene was taken in a titration flask containing 70 ml CHCl3. 9.0 grams of FeCl3 was weighed and 180 ml CHCl3 was added to this. This solution was stirred using magnetic stirrer and added to the solution of thiophene in CHCl3. To this whole PVA thin film was added in the ratio of (1:2). The whole reaction mixture was homogenized and kept in a petri dish (corning glass, 2.5" diameter) maintained at 35 ± 0.2°C for 24 h.
Ammonium persulfate (APS, 8.20 g) was dissolved in 20 mL deionized water. Then the ammonium persulfate solution was added dip into the rectangular size piece semi-transparent film. The mixture was heated without stirring (oven) for 5h at 70°C.

Thereafter the oven switched off and allowed to cool at the room temperature. The resulting thin film was collected by filtration or centrifugation. It was washed by deionized water and then freeze-dried for 24 h. As the polymerization progresses, the semi-transparent film turns into light brown, which can be isolated by filtration. During the course of the reaction, the film changed from dark brown (Figure 7).

III. RESULT & DISCUSSION

FT-IR (Fourier Transform Infrared Spectrometry)
To identify the chemical functional groups present and the miscibility of the polymers in film. FTIR considered to be a powerful tool and potentially very widely applicable method. The Fourier Transform Infrared spectroscopy (FTIR) spectra of pure and polythiophene doped PVA films were obtained and the results are shown in Figures 8,9. The spectra show a strong broad absorbance at 3670 cm\(^{-1}\) for pure PVA and 3657 cm\(^{-1}\) for 2% polythiophene doped PVA. This band could be assigned to O-H stretching vibration of hydroxyl group of PVA, the band corresponding to C-H asymmetric stretching vibration occurs at 2960 cm\(^{-1}\) and 2949 cm\(^{-1}\) for the doped PVA. The band at 1753 cm\(^{-1}\) corresponds to C=O stretching vibration and remains the same for 2% dopant and shifted toward 1761 cm\(^{-1}\).
UV (Ultraviolet) spectroscopy

Ultraviolet spectroscopy has been used to study the absorption, measures transition from the ground state to excited state. In this, sample is exposed to the light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges and the response is monitored. The absorption or reflectance in the visible range directly affects the perceived colour of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions.

“Typical” UV-VIS instrument

UV absorption of film sample-1 and sample-2 are obtained by UV-Spectroscopy Instrument name-Cary Varian. This technique is completely for absorption, measures transition from the ground state to the
excited state using the wavelength of detection 200-800 nm and the methanol solvent for determination is used. Thus, thus the absorption peak can be studied with respect to wavelength.

UV radiation interacts with matter which causes electronic transition (promotion of electrons from the low energy state to high energy state) UV region falls in the range between (190-390nm). For the determination of concentrations of an absorbing species in solution this method is frequently used, using the Beer- Lambert law: $\log_{10}(\frac{I_0}{I})$ Where A is the measured absorbance, in Absorbance Units (AU). UV absorption spectra of pure PVA are found wavelength 215 nm and absorption 3.4578 are shown in Figure 7. UV absorption spectra Polythiophene doped PVA film for sample-2 are shown in Figure(10).

No absorption in the range 316-500 nm was observed for the undoped PVA films but as the doping percentage increase, the absorbance was also increased showing a broad peak appeared at 325 nm.

![Figure 9: UV-visible spectrum of Pure PVA Sample-1](image)

![Figure 10. UV-visible spectrum of Polythiophene doped PVA film (sample-2)](image)
The UV-Vis spectroscopy is a valuable and simple method for quantitative analysis, offered by the Beer-Lambert law. The UV spectroscopy is widely used in determining equilibrium constant rates, acid-base dissociation constants, and other properties for chemical reactions. The UV-Vis spectroscopy has many applications in the pharmaceutical and drug industry. The use of UV-Vis spectroscopy in the evolution of enzymatic assays has become very common.

IV. APPLICATION

The polythiophene can be water soluble, water dispersible, or water swellable. They can be self-doped. The organic substituent can be an alkoxy substituent, or an alkyl substituent. OLED, PLED, SMOLED, PV, and ESD applications can be used. Although useful advances are being made in energy-saving devices such as organic-based organic light emitting diodes (OLEDs), polymer light emitting diodes (PLEDs), and organic photovoltaic devices (OPVs), further improvements are still needed in providing better processing and performance. This unique combination of properties has given these polymers a wide range of applications in the microelectronics industry, including battery technology, photovoltaic devices, light emitting diodes, and electrochromic displays (reviewed in and more recently in the biological field).

V. CONCLUSION

It reports on the successful electrochemical preparation of Polythiophene poly(vinyl alcohol) (PThs-PVA) composite films by direct or one-step polymerization method in aqueous medium. The XRD technique indicates that the film possesses amorphous nature (i.e.,) disorder in polymer chains. The hydrogel composite shows cluster-like morphology varying in size between 0.5 to 2.0 μm. The polythiophene (PThs) particles undergo aggregation and show a wide variation in their sizes ranging from 1 to 100 μm. SEM micrographs report the shape and size of the developed molecules form clusters of polythiophene on the PVA thin film which mainly affects the electrical and optical properties of the polymer films.
REFERENCES