

Synthesis & Characterization of Nanomaterial 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, XRD, SEM, conducting Polymers (Thin films), Spectroscopy.

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, thermosets, elastomers and synthetic fibers. They are found commonly in a variety of consumer products such as money, super glue, etc.^[1] Polyvinyl alcohol (PVOH, PVA, or PVAI) is a water-soluble synthetic polymer (not to be confused with polyvinyl acetate, a popular wood glue). It has the idealized formula $[\text{CH}_2\text{CH}(\text{OH})]_n$. 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^[2]. 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^[3].

Thiophene, also commonly called thiofuran, is a heterocyclic compound with the formula C_4H_4S . 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 (C_4H_4O) and pyrrole (C_4H_4NH). Thiophene was discovered as a contaminant in benzene. This new heterocyclic compound was thiophene^[5]. Polythiophenes become electrically conductive upon partial oxidation, i.e. they become "organic metals"^[4]. Polythiophene has been widely used in environmentally and thermally stable conjugated polymer 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^[7]. For example structure of poly-acetylene is shown in figure (1)

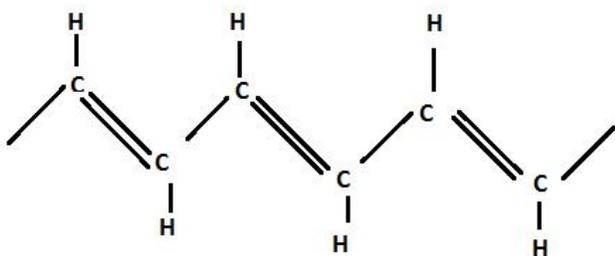


figure (1) Structure of poly- acetylene

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

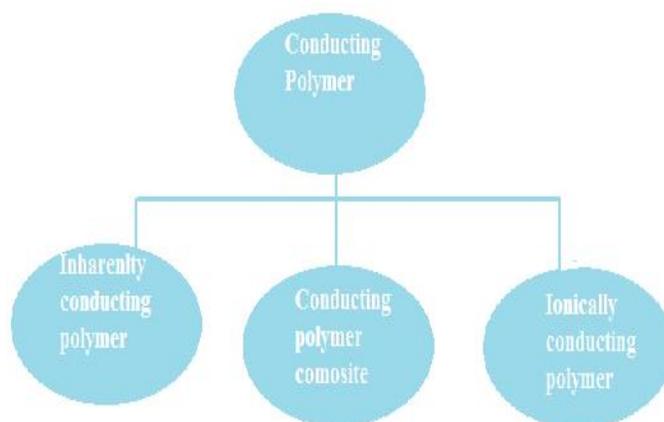


Figure (2) Classification of conducting Polymer

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 10000 g/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 $20 \pm 0.05 \mu\text{m}$.

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



Image (4) Thin films of Pure PVA

Polythiophene doped PVA thin film (sample -2)

Synthesis of PTh :-Two milliliter of thiophene was taken in a titration flask containing 70 ml CHCl_3 . 9.0 grams of FeCl_3 was weighed and 180 ml CHCl_3 was added to this. This solution was stirred using magnetic stirrer and added to the solution of thiophene in CHCl_3 . 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 $35 \pm 0.2^\circ\text{C}$ for 24 h.



Figure (5) Solution is cast on polythiophene doping PVA thin film

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 (image 6), which can be isolated by filtration. During the course of the reaction, the film changed from dark brown (image7).

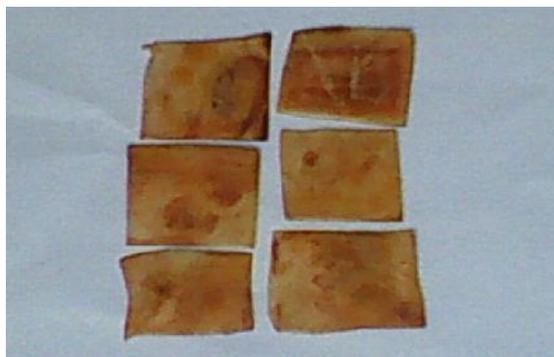


Image (6) Films of PTs doped PVA (sample 2)



Images (7) Films of PTs doped PVA (APS solution dip sample 2)

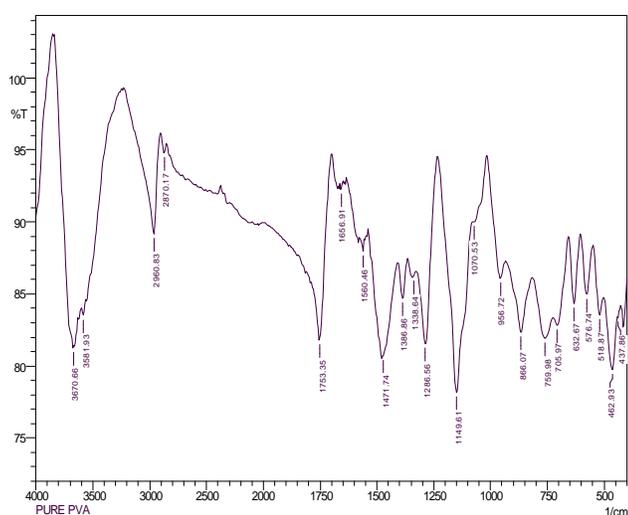
III. RESULT & DISCUSSION

FT-IR (Fourier Transform Infrared Spectrometry)

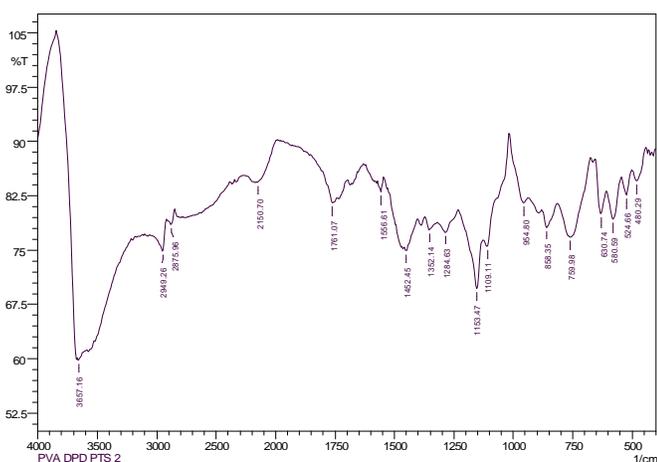
To identify the chemical functional groups present and the miscibility of the polymers in film. FTIR considered

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=C stretching vibration and remains the same for 2% dopant and shifted toward 1761 cm^{-1} .



Figure(8) FTIR spectra of pure PVA thin films.



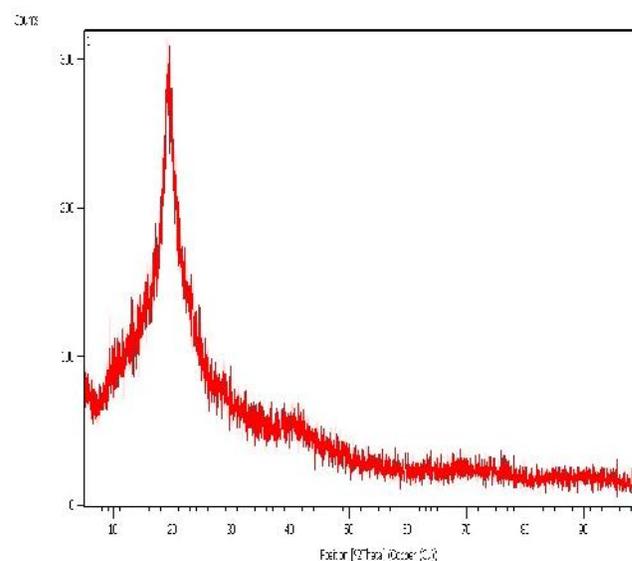
Figure(9) FTIR spectra of polythiophene doped PVA thin film

X- Ray Diffractometer Analysis

The experimental method and results of XRD study carried out on films sample-1 and sample-2 are discussed in this section. X-ray diffraction (XRD) has been utilised to detect change in crystalline and amorphous characteristics in the films. A brief account of XRD study, its application area, calculation of crystallite size, plane and other concept related to the present investigation are also presented.

The pure PVA showed a characteristic peak for an orthorhombic lattice centered at $2\theta, 20^\circ\text{C}$ indicating a semi crystalline nature (Fig.10). Peaks at 11 and 20 were due to PVA. The amorphous nature of the PVA thin films doped with Polythiophene were investigated by XRD analysis using Smart Lab x-ray diffractometer having Cu-K source (1.54 \AA).

The various specification and optimized experimental parameters of XRD system used to have the x-ray diffraction of PVA films have been tabulated in figure(10). The amorphous characteristics of the PVA membrane is found to be two discernible peaks at $2\theta \sim (8.557965(14))^\circ, (20.01096514)^\circ$ respectively that have been clearly observed in (Fig.11) respectively.



Figure(10) XRD-spectra of pure PVA thin films.

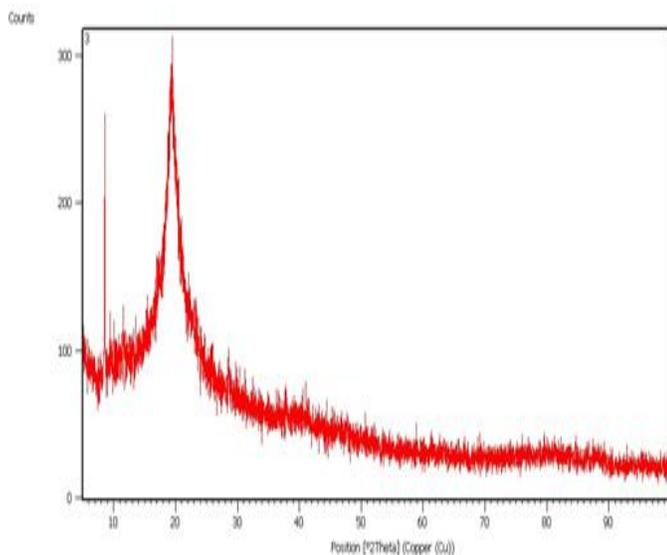


Figure (11) XRD spectra of Polythiophene doped PVA thin films.

SEM (Scanning Electron Microscopy)

Scanning Electron Microscopy (SEM) micrographs help to study the complete chain formation with texture and other features of developed nano-domain structures, in the pure and composites. The SEM images of PVA and the composite PVA-PThs were shown in the images 12,13 respectively. The SEM visualizes the presence of small ratio of secondary phase (PThs) which was randomly distributed and get adhered on PVA matrix.

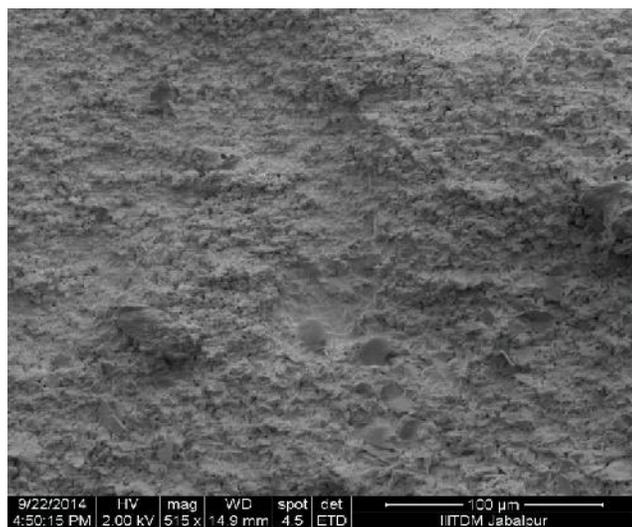


Figure (12) SEM image of PVA thin film

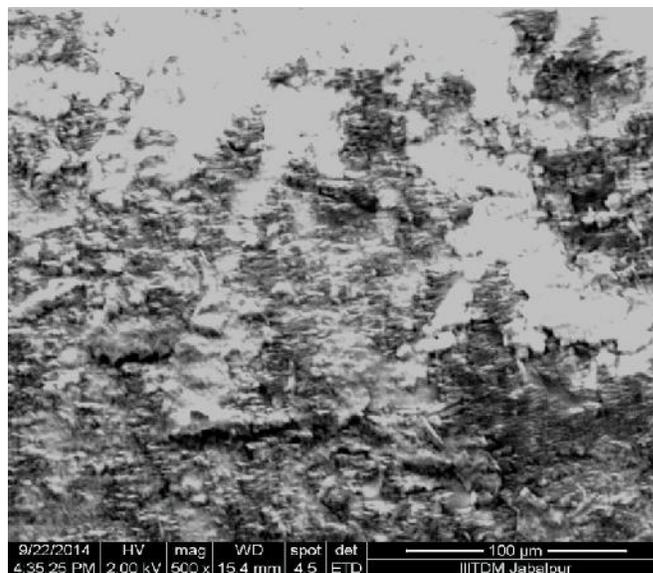


Figure (13) SEM image of Polythiophene doped PVA thin film

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 report 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.

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