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Optical and Fluorescence Study of Ethidium Bromide Doped Poly (Vinyl Alcohol)

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Abstract— The effect of Ethidum Bromide (EtBr) dye on microstructural and optical properties of the polymer Poly (vinyl alcohol) (PVA) is studied. The FTIR study shows the appearance of new peaks, indicates the interaction of EtBr with PVA. UV-Visible spectrum show three peaks (around 215nm, 285nm and 480nm) and corresponding three optical energy band gaps. Fluorescence emission spectra observed in the region 600nm for 500nm excitation. These results are understood based on charge transfer complex (CTC) formation. Variation in the fluorescence anisotropy (r=0.36-0.87) of the composite films indicate the Ethidium Bromide molecular motion is suppressed in the solid polymer films. The fluorescence microscopic image of these composite films shows that the films are photochromic in nature.

Keywords— Ethidium Bromide; Charge complex transfer; Fluorescence.

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1. INTRODUCTION

Chromophore doped polymer is one of the most promising materials for potential applications like optical devices, such as optical fibers, nonlinear optics, optical storage, optical information processing and optical switches, because of its unique properties and reasonable cost performances [1, 2] which makes the dye-doped polymer films very suitable for optical devices. The possibility of organic dye doped polymers for optoelectronics applications is not limited and developments of new organic polymers more promoted.

Poly(vinyl alcohol) (PVA) has unique chemical and physical property like non-toxicity, water-soluble, biocompatible, and biodegradable synthetic polymer and used in many applications in industrial sector, pharmaceutical and medical fields. It is a semicrystalline polymer, has very important applications due to the role of OH groups and hydrogen bonds [3, 4]. Ethidum Bromide (EtBr) is an intercalating agent. It has been used widely for various biochemical and biophysical applications [5]. EtBr is donar and acceptor type dye considered to be most important materials for wide applications in photonics [4, 6]

2. EXPERIMENTAL

The polymer PVA used in this work is obtained in powder form from M/s. s.d. fine-Chem. Ltd, Mumbai. The EtBr doped PVA films were prepared by solution casting method using distilled water [2]. The FTIR

Corresponding Author Phone: +91 9449681234; Email: naik 40@rediffmail.com spectra of the prepared films were obtained using NICOLET FTIR-6700. UV-Vis study was performed using SHIMADZU (UV-1601) spectrometer in the wavelength range 195-700nm. The fluorescence measurements were conducted using Hitachi F-7000 fluorescence spectrophotometer. Fluorescence images of the films were taken using AXIO imager.

3. RESULT AND DISCUSSIONS

3.1 FTIR Studies

The observed IR spectra of pure and EtBr doped PVA are as shown in Figure 1. From the Figure it is observed that the broad band at 3436cm⁻¹ is assigned to O-H stretching vibrations of PVA and shifts from 3436 cm⁻¹ to 3440cm⁻¹ for the PVA/EtBr composite, attributed to N-H stretching



Fig. 1: FTIR Spectra of the pure and EtBr doped PVA

vibrations. 2923cm⁻¹ band assigned to C-H symmetric stretching and the band observed at 2923cm⁻¹ for pure PVA shifts to 2920 cm⁻¹ to 2930cm⁻¹ with increasing intensity and become sharper.

The band at 1318 cm⁻¹ for pure EtBr corresponding to Ph-N (CH₃)₂ stretching vibration are shifting to 1318-1370cm⁻¹ with increase in intensity. For pure EtBr, the N-H (NH₂) stretching vibration at 1030 cm⁻¹ and shifted to 1032 cm⁻¹ with increasing intensity. These variations in IR results are understood by invoking the hydrogen bonding and hydrophobic interaction between the PVA and EtBr and formation of charge transfer complex, which modifies the microstructural properties of PVA [4, 5].

3.2 UV-Vis Absorption Studies

The effect of PVA on the optical absorption spectra of EtBr investigated at different dye concentrations as show in Figure 2.



Fig. 2: UV-Visible absorption spectra of Pure Ethidium Bromide doped PVA.

The Figure shows that there are three absorption peaks (around 215nm, 285nm and 480nm) for the doped PVA. The peak-I arises due to the presence of carbonyl group containing segments (C=O and/or C=C) in the tail-head of PVA. Peak-II is assigned to $n \rightarrow \pi^*$ interband transition and attributed to the excitation in the aromatic rings and phenyl groups of EtBr present within the composite films. Both these peaks will shows bathochromic shifts attributed to the interaction of NH₂ groups of EtBr with OH group of PVA [6]. The absorption peaks-III may be arises due to the charge transfer groups and assigned to $\pi \rightarrow \pi^*$ transition and shows hypsochromic shift, may be due to the hydrophobic interaction between $N(C_2H_5)$ group of EtBr with the hydrocarbon group of PVA, understood based on CTC formation. The corresponding three optical band gaps are E_{g1} (4.96–4.80eV) E_{g2} (3.61– 3.30eV) and E_{g3} (1.94–1.80eV).

3.3 Fluorescence Studies

The Fluorescence emission spectra of EtBr doped PVA films for 500nm excitation is shown in the Figure 3 and the fluorescence emission peak wavelengths and intensity

increases with EtBr concentration. The fluorescence microscopic image is shown in the inset of the Figure 3.



Fig. 3: Fluorescence emission spectra of EtBr doped PVA

From the Figure it is observed that for the excitation wavelength of 450nm the composite films emit red color in the region of 600nm. This property of emission may be due to the aromatic NH_2 and phenyl groups present in EtBr. The cationic molecules weakly fluorescent in water, when these interact with the poly nucleotides or polymer and fluorescence intensity increases. The increasing EtBr concentration in PVA results in shifting of the peaks towards the red region by 8nm (>620nm) and fluorescence band became broaden can be ascribed to formation of aggregated species with increasing concentration of EtBr [8].

Fluorescence microscopic images of EtBr doped PVA films are shows the photochromic effect and varies with dopant concentration leads to the changes of chemical bond or the motion of molecular segments. This photoinduced electron transfer reaction is mainly from a donor to an acceptor and it can be utilized for optical devices and optical storage applications etc. This fluorescent behavior of EtBr dye molecules within the PVA matrix shows gradually enhanced emission suggests the "aggregation-induced enhanced fluorescence emission" [5]

The estimated fluorescence anisotropy for EtBr doped PVA is from 0.36 to 0.87 for 250nm nm excitation is shown in Figure 4.



Fig. 4: Variation of fluorescence anisotropy r EtBr dope PVA for $\lambda_{ex} = 550$ nm

From this decay curve observed that depolarization is also occurred in the PVA matrix which is caused by the energy migration between EtBr molecules [8]. These results suggest that the EtBr molecular motion is suppressed in the solid polymer film. That means the EtBr chromophore molecules in PVA matrix are more rigid and the anisotropy may be zero. During excitation the motion of a chromophore is fast enough or excitation energy can hop among the molecules, as a result the anisotropy of the emission falls to zero or nearer to zero

4. CONCLUSION

Variations in the spectral results are understood by invoking the hydrogen bonding and hydrophobic interaction between the PVA and Ehidium Bromide and formation of CTCs. The fluorescence imaging shows that the composite films are photochromic in nature. This property can be utilized for optical devices and optical storage applications etc.

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