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Measurement of optical properties of poly (vinyl-alcohol) polymer thin films

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ABSTRACT
Solvent casting was used to create films of Poly (vinyl alcohol) polymer that were doped with pure and chalcone derivative crystals. Utilizing measurements of the refractive index, steady state fluorescence, and UV-Vis optical absorption, the optical characteristics of these films were examined. The composite films' reported UV-Vis absorbance maximum at 273 nm was attributed to the high-energy absorbance of the carbonyl group i.e., $n \rightarrow \pi^*$ transition, while the 427 nm band was attributed to the $\pi \rightarrow \pi^*$ transition, which results from excitation in the aromatic ring and charge transfer band (C = O group). According to UV-Vis spectra, the optical energy band gap for pure PVA is calculated to be 4.78 eV. It reduces with increasing doping concentration and reaches 2.25 eV for pure compound. In order to evaluate the fluorescence emission spectra, the films were excited at 273 nm and 427 nm. Two fluorescence emission bands around 426 nm and around 512-540 nm for 427 nm excitation exhibit a wide bandwidth of 200 nm, while the detected fluorescence emission bands are around 514-550 nm for 273 nm excitation (450-650 nm). Using Brewster's angle method, it was shown that the composite films' refractive indices fall between 1.516 and 1.519 for red He-Ne lasers with a wavelength of 632.8 nm and 1.519 and 1.525 for green He-Ne lasers with a wavelength of 543.5 nm. The hydrogen bonds and hydrophobic interactions between the OH group of PVA and the CO, CH₃, and N(CH3)₂ groups of the chalcone derivative are the primary causes of all these alterations inside the PVA matrix caused by doping.

1. Introduction

Due to its primary role in the development of useful photonics devices such holographic image recorders, wave-guides, electro-optic memory, data storage devices, etc., optical characteristics of chromophore doped polymers have gained attention during the past two decades [1]. It is well known that the side group or side-group ratio caused by doping with a chromophore can be changed to tailor the polymer characteristics required for such specialised optical applications. In this situation, the characteristics of such materials ought to be significantly influenced by the interactions between the polymer and the chromophore [2]. To adjust the optical property, different chromophores are doped into a polymer. PVA, or poly (vinyl alcohol), is a polymer with a number of intriguing physical characteristics, including effective film formation. The presence of an OH group within the polymer chain is primarily responsible for these features. When the chromophore is doped into PVA, the dopant engages in hydrogen bonding with the hydroxyl groups to form donor-acceptor moieties. The chromophore's donor-acceptor moieties frequently affect the optical properties, especially the UV absorption and fluorescence emission [3-5]. In light of this, the aim of present article is to determine how chalcone derivative 1-(4-methylphenyl)-3-(4,N,N-dimethylaminophenyl)-2-ropen-1-one doping affects the optical characteristics of PVA. This is done by utilising techniques for UV-Visible, Fluorescence, and Refractive Index Spectroscopy.

2. Materials and sample preparation

The average molecular weight of the PVA employed in this study is 1,25,000. The structure of the newly synthesised 1-(4-methylphenyl)-3-(4,N,N-dimethylaminophenyl)-2-ropen-1-one (MPDMAPP), an organic non-linear optical chromophore, is shown in Figure 1. N, N-dimethylformamide (DMF) was used as general solvent during solution casting process to create the pure/MPDMAPP doped PVA films [7]. The created composite films have a light orange tint and are transparent.
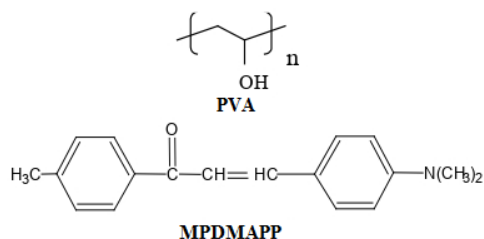

Figure 1. Structure of MPDMAPP/PVA

3. UV-Vis studies

The SECOMAM ANTHELIE-284 UV-VIS Spectrophotometer was used to conduct optical studies on the pure PVA and PVA/MPDMAPP composite films in the

wavelength range of 195 -1000 nm. Figure 2 displays the acquired UV-Vis absorption spectrum for both pure and MPDMAPP-doped composite films.
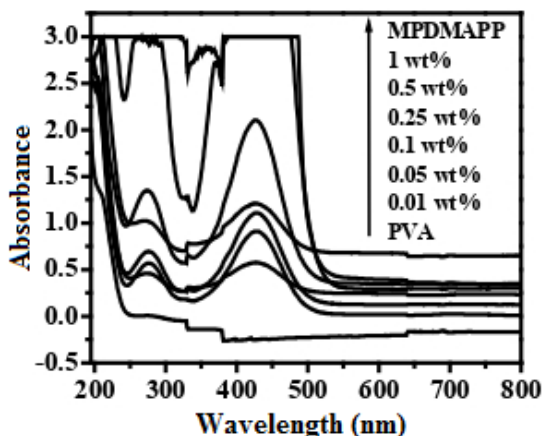

Figure 2. UV-Vis spectra

The figure depicts the absorbance band for pure PVA at 196 nm, and it may be recognized as $n \rightarrow \pi^*$ transition of unsaturated bonds with tail-head positions of $C = O$ and/or $C = C$. Three absorption bands are seen for the composite films. The first band, which is located between 196 and 210 nm, is attributable to carbonyl-containing segments in the UV region and is referred to as localised $n \rightarrow \pi^*$ transitions. The second is classified as the $n \rightarrow \pi^*$ inter band and is between 250 and 350 nm. This band is due to the excitation of the phenyl groups of MPDMAPP found in the composite films, as well as aromatic rings and $C = O$ groups. The charge transfer groups may be cause of third band, which is roughly 375–525 nm in wavelength. According to the UV-Vis spectra, the composite films' absorption peaks (λ_{max} = 428 – 426 nm) and absorption edges exhibit a blue shifting along the smaller wavelengths as well as an observed increment in intensity when chalcone concentrations rise. The dominance of $\pi \rightarrow \pi^*$ transitions and the development of complexes via intermolecular hydrogen bonding are indicated by the blue shift that is the result of doping. The interaction of the MPDMAPP molecule with hydroxyl groups of polymer as well as the formation of the charge transfer complex can be used to explain the aforementioned alterations in the UV-Vis spectra. When the MPDMAPP is doped with PVA and the loose complexes are permissible to mingle, one of these acting as an electron-acceptor and the other as an electron-donor, and they combine to form a donor-acceptor complex. In this case, MPDMAPP contains both donor and acceptor groups with electrons. Donor-acceptor and electron-donor complexes will be produced as a result of the doping in the composite. Additional charge-transfer absorption bands follow from excitation of these electrons to upper, empty molecular orbital of acceptor. As a result, the aromatic carbonyl compounds exhibit absorption bands that can be classified as $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and charge transfer transitions. New energy band gaps are anticipated when such extra bands are present in the PVA that has been doped with chromophore. By transforming the obtained UV-Vis spectra into Tauc's graphs (Figure 3), the author was able to determine the optical band energy gap E_g in order to take this into consideration [7].
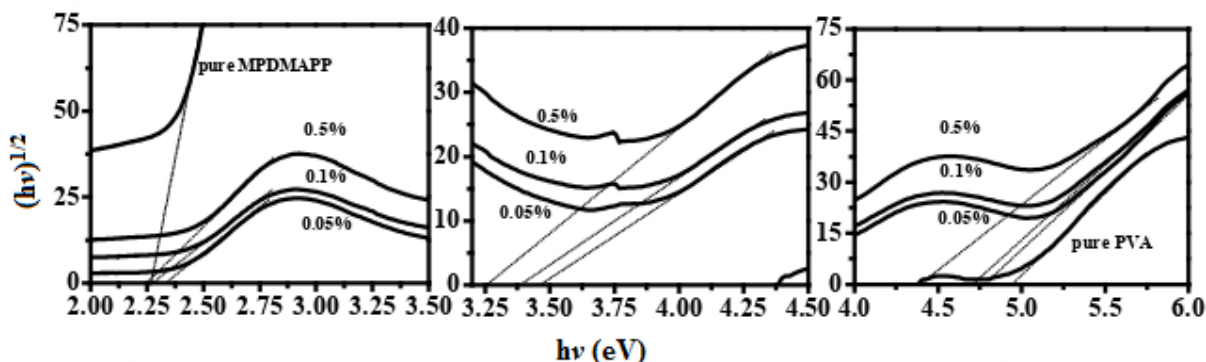

Figure 3. Optical bandgap of MPDMAPP/ PVA composite films

According to Figure 3, optical energy band gap in case of pure PVA is expected to be 4.78 eV, while that for pure MPDMAPP chalcone is 2.25 eV. We found three zones for each of the three optical absorption edges in PVA/MPDMAPP composite films, which is consistent with other researchers' findings [8]. Higher optical energy gap E_{g1} (4.70–4.14eV), moderate optical energy gap E_{g2} (3.45–3.25eV), and smaller optical energy gap E_{g3} are characteristics of these absorption edges (2.35 - 2.20 eV). The optical band gap is less than pure PVA in this instance and declines with dopant concentration, reaching 2.25 eV for pure MPDMAPP. This fluctuation in the composite films' Eg values suggests that new groups for optical transitions are produced as a result of MPDMAPP's interaction through hydrogen bonding with OH group of PVA. As a result, MPDMAPP doping causes a change in the polymer's microstructural behaviour.

4. Fluoresence measurements

Fluorescence Spectrophotometer was used to conduct the steady state fluorescence emission spectral research. The samples are excited at 273 nm and 427 nm using a 500 W Xenon lamp (λ = 220 - 800 nm), and the fluorescence emission has been monitored. The UV absorption of the film is corresponding to this excitation wavelength. The films' fluorescence microscopic images were captured using a fluorescence microscope that had a 40X magnification. Here, the fluorescence excitation was carried out utilising the mercury lamp of power 100 W through a U-excitation

filter (U-MWB) BP 450-480 and a G-excitation filter (U-MWG) BP 510-550 that permits light of wavelengths 450 nm to 480 nm and 510 nm to 550 nm wide bands to pass, respectively. Figure 4 depicts the composite films'

fluorescence emission spectra. We can see in the figure that the fluorescence emission intensity rises as the excitation wavelength and dopant concentration both rise.
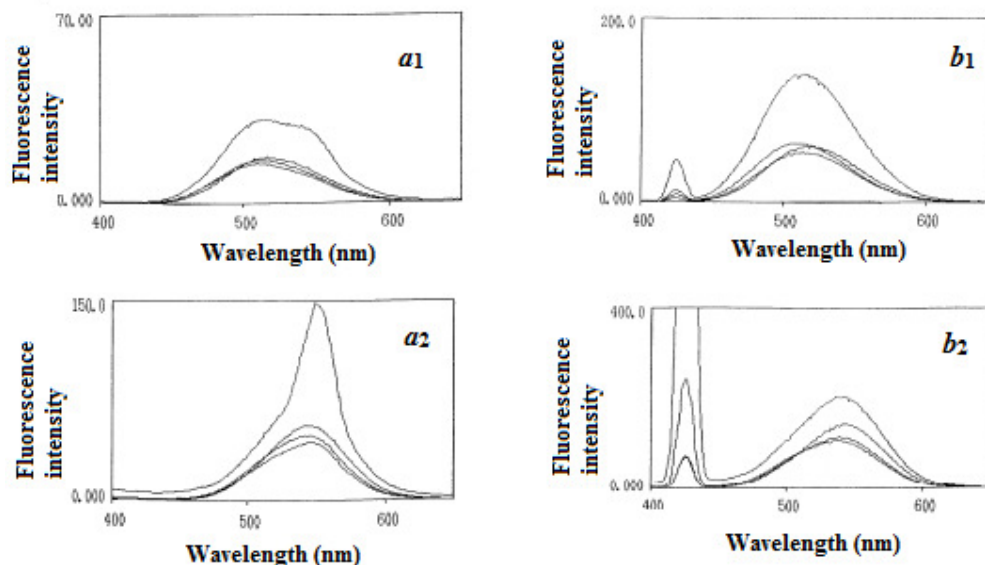

Figure 4. Fluorescence emission spectra of the PVA/MPDMAPP composite with the excitation wavelength of (a) 273 nm and (b) 427 nm (a_1, b_1 = 0.05 wt % and a_2, b_2 = 0.5 wt % dopant concentrations)

Up to 0.5 weight percent chalcone concentrations, we found a stokes shift in emission wavelengths (λ_{max}) from 512 to 540 nm for 427 nm irradiation and from 514 to 550 nm for 273 nm illumination, along with an increase in the fluorescence emission peak strength for the doped samples (Figure 5 a, b). The maximal emission max has a 1 weight percent hypochromic shift toward the blue. This intense fluorescence emission in this region (λ_{max} = 514 – 550 nm) may originate from the complex's C–C bond and result from the interaction of chalcone and PVA with hydrogen bonds.

Due to the particular intermolecular interactions between the chalcone moieties and OH groups of PVA, the observed change results suggest that the chalcone molecules in the crystalline shape are lesser luminous but intensely fluorescent in polymeric matrix configuration. The fluorescence chalcone molecules in PVA exhibit "aggregation-induced enhanced fluorescence emission," or gradually enhanced fluorescence emission with increasing concentrations. One feeble emission is seen at wavelength

of 426 nm at an excitation wavelength of 427 nm, in addition to this robust emission. The strength of this emission peak is modest at smaller dopant concentrations (0.05 wt%) and increases at larger dopant concentrations (0.5 wt%). Higher dopant concentrations result in dominance of 426 nm wavelength emission peak, which demonstrates the strong hydrophobic interactions between the OH and hydrocarbon portions of PVA and the CO, CH_3, and $N(CH3)_2$ groups of chalcone derivatives. These interactions, combined with hydrogen bonding, result in charge transfer groups. It is possible to investigate the device application of the observed fluorescence emission spectra at higher wavelength, high fluorescence quantum yield for low excitation light, and a red shift with rise in chalcone concentration. Owing to its transparency in visible regime, higher value of extinction coefficient in UV regime, and exceptional stability, chalcone compounds have been used as fluorescent dyes and UV light stabilisers.
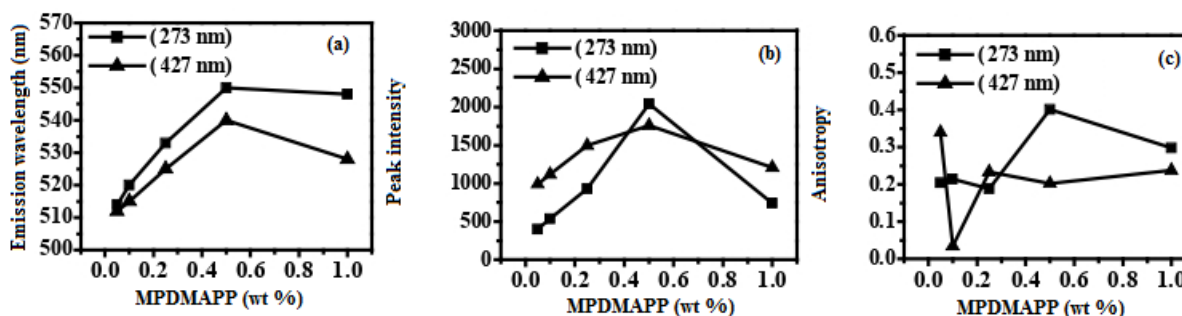
Figure 5. Variation of (a) Fluorescence emission peak wavelengths, (b) peak intensity, and (c) anisotropyof MPDMAPP/PVA composite films v/s MPDMAPP concentration for λ_{ex} = 273 nm and λ_{ex} = 427 nm

Equation (1) estimates fluorescence anisotropy or the degree of polarisation *r*.

$$r = (I_{VV} - I_{VH})/(I_{VV} + 2I_{VH}). \tag{1}$$

In Eq. (1), I_{VH} and I_{VV} stand for horizontally and vertically polarised fluorescent light, respectively which is made from excitation light with a vertical polarisation. Figure 5c displays the predicted fluorescence anisotropy of the PVA/MPDMAPP composite at various concentrations for the two excitation wavelengths.

For excitations of 273 nm and 427 nm, respectively, the estimated fluorescence anisotropy of pure chalcone is determined to be 0.086 and 0.081, respectively. The fast molecular mobility of chalcone molecules in solution at room temperature is explained by the low value of anisotropy in pure chalcone. For composite films, it varies from 0.2 to 0.3 for excited wavelength 427 nm and from 0.17 to 0.4 for excited wavelength 273 nm. R's analytical outcome lies between -0.2 and 0.4. Solid films typically have suppressed molecular movements and zero anisotropy. However, in our situation, we noticed a slight anisotropy, suggesting that the chalcone molecules can enter the polymer's free volume holes. Therefore, it makes sense to predict that if chalcone concentrations were increased, the perceptible anisotropy value of composite films would also increase. For a given amount of empty space, we would anticipate that larger chalcone molecules will move more slowly than smaller chalcone molecules. There is some quantifiable distribution of the potential volume of such spaces, which is free volume whose size in polymer is larger than the chalcone molecule. This is comparable to one shown in Reference [9].

Figure 6 displays the fluorescent microscopic pictures of chalcone-doped (0.5 wt%) PVA film. Red emission under green wide band pass excitation (510–550 nm) and Bright green emission under blue wide band pass excitation (450–480 nm) sources, respectively, are visible in the fluorescence microscopic picture of these films. The aromatic C = C and phenyl groups found in chalcone chromophore may be responsible for its emission under excitation property's long-lasting nature.
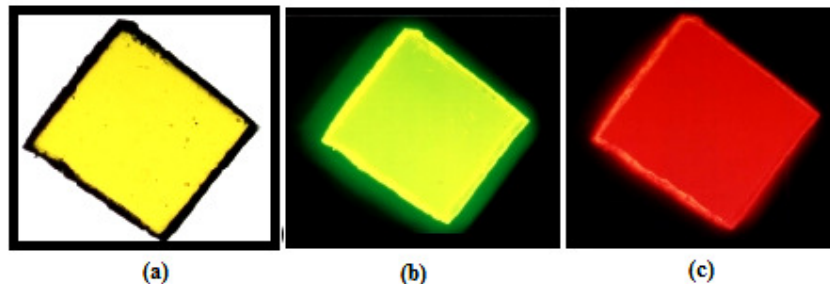
Figure 6. Fluorescent microscopic pictures of the composite film (0.5 wt%) are shown in (a) room light, (b) excitation emitting strong green light at 450–480 nm, and (c) excitation emitting red light at 510–550 nm.

Thus, the composite films' photo-induced fluorescence produced vivid fluorescent pictures, suggesting that the intra-molecular hydrogen bond is important for the function of chalcone doped PVA. The ultra-quick response time of this photo-induced electron transfer reaction from a donor to an acceptor makes it advantageous for optical memory, optical switching, and optical data storage devices.

5. Refractive index

Brewster's angle technique and $n = \tan \theta_{P}$, in which θ_P is polarising angle, were used to calculate the indices of refraction of composite films. The determined value of index of refraction of MPDMAPP crystal is 1.465, whereas the index of refraction for PVA/MPDMAPP composite films varies from 1.516 to 1.519 for the Red He-Ne laser (λ = 632.8 nm). This demonstrates that as the dopant concentration rises, films' refractive indices do as well. This change in refractive index brought on by doping reveals a molecular alteration in the side-group ratios or polymer side-groups. The aromatic C = C of the chalcone and the CO, CH_3, and $N(CH3)_2$ groups may have an impact on indices of refraction of the composite film. These groups form as a result of intermolecular interactions, such as hydrogen bonds and hydrophobic interactions between the OH and hydrocarbon parts of PVA. The UV-Vis absorption research is consistent with these refractive index values.

6. Conclusions

Using UV-Vis optical absorption, Steady State Fluorescence, and Refractive Index measurements, the impact of chalcone derivative doping on the optical property of the poly(vinyl alcohol) has been investigated. According to the UV-Vis absorption investigation, the dopant forms new charge transfer groups through hydrogen bonding with the polymer's OH group. These groups influence the microstructure, which in turn influences the band gap and, as a result, the fluorescence property and refractive index of the PVA.

References

[1] A.M. Albu, V.M. Tarpa, Polymer Architectures for Optical and Photonic Applications, in: *Nonlinear Optics*, B.I. Lombrikov (Ed.) Intech Open, UK (2021).

[2] P.C. R. Kumar, K. Janardhana, K.M. Balakrishna, T. Sheela, Study of nonlinear optical properties of a chalcone doped PVA composite material, *Proc. Eng*. **141** (2016) 83-90.

[3] K.D. Belfield, K.J. Schafer, A new photosensitive polymeric material for WORM optical data storage using multichannel two-

photon fluorescence readout, *Chem. Mater*. **14** (2002) 3656-3662.

[4] J.K. Lee, H.J. Kim, T.H. Kim, C.H. Lee, W.H. Park, J. Kim, T.S. Lee, A new synthetic approach for polybenzoxazole and light-induced fluorescent patterning on its film, *Macromolecules*, **38** (2005) 9427-9433.

[5] B. Zhou, Y. Lin, L.M. Veca, K.A.S. Fernando, B.A. Harruff, Y.P. Sun, Luminescence polarization spectroscopy study of functionlized carbon nanotubes in a polymeric matrix, *J. Phys. Chem. B* **110** (2006) 3001-3006.

[6] V. Ravindrachary, V. Crasta, RF. Bhajantri, B. Poojari, Growth and characterization of chalcone derivative single crystal, *J. Cryst. Growth* **275** (2005) e313-318.

[7] R.F. Bhajantri, V. Ravindrachary, V. Crasta, S.P. Nayak, B. Poojary, Microstructural studies on BaCl$_2$ doped poly(vinyl alcohol), *Polymer* **47** (2006) 3591-3598.

[8] H.M. Zidan, M. Abu-Elnader, Structural and optical properties of pure PMMA and metal chloride-doped PMMA films, *Physica B* **355** (2005) 308-317.

[9] H. Itagaki, J. Mochizuki, Size and distribution of free volume in thermoreversible gels of syndiotactic polystyrene, *Macromolecules* **38** (2005) 9625-9630.