

## **UV-VISIBLE PHOTODEGRADATION OF METHYLENE BLUE DOPED IN POLY(VINYL ALCOHOL)(PVA) SOLID MATRIX**

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### **ABSTRACT**

In this paper, The photobleaching of methylene blue (MB) doped in poly(vinyl alcohol) (PVA) matrix was investigated using an uv-visible fibre optic spectrophotometer. The absorption observed at 660nm decreases with the increasing of the exposure time. The blue color of the MB doped PVA sample turned completely colorless after irradiation for 360 seconds. The optical transmission of the samples at different dye concentration was measured in the range of 450-800nm. The photobleaching mechanism in the present sample was also discussed. The experimental results shown that the material studied could be a good candidate for waveguide devices.

### **INTRODUCTION**

Light has many properties, such as wavelength, polarization and coherence. In order to increase further the memory density in optical recording system, so-called photon mode optical memories, employing photochemical reactions, instead of thermal reactions, and currently used in optical discs, are being developed. Recently, holography finds very wide application in the fields of technology, the most recent being the usage of holograms as memory elements. Optical storage of data has been one of the bright spots in technology over past 15 years. Without a doubt, optical memories store huge amounts of digitized information inexpensively and conveniently. Holographic memories, it is now believed, could conceivably store hundreds of billions of bytes of data, and transfer them at a rate of a billion or more bit per second and select a randomly chosen data element in 100  $\mu\text{m}$  or less [1,2].

The future development of holography mainly depends upon the development of an inexpensive and real time holographic recording media. Many materials have been tried and many new ones are being tried. One of such material is dye sensitized polymer film. New holographic recording materials based on the dye-polymer systems have contributed significantly to the recent growth of holographic applications [1].

One of the most used dyes is methylene blue (MB) with the chemical formula ( $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ ). MB is a blue thiazine dye with wavelength ( $\lambda_{\text{max}}$ ) value at around 660nm. It is a popular dye sensitizer in photochemistry, especially in the areas of reductive electron transfer and singlet oxygen production. MB has been used for formation of high spatial frequency amplitude and phase holograms with a conventional He-Ne laser as a light source. The principal mechanism of grating formation is photobleaching of MB in a matrix [3].

The photobleaching of methylene blue (MB) when exposed to electromagnetic radiation is a well-known phenomenon. Colored MB dye molecules is photoreduced by uv-visible light producing leuco form of MB. In a pure form, MB cannot be photobleached; it is necessary to put its molecule into a suitable optical quality matrix. In this paper, we have selected methylene blue sensitized polyvinyl alcohol (PVA) matrix for our study. The mechanism of photobleaching of methylene blue doped in PVA matrix is investigated in details using an uv-visible fibre-optic spectrophotometer (OCEAN Optics, S2000).

Polyvinyl alcohol (PVA) with a general formula  $[-\text{CH}_2\text{CH}(\text{OH})-]_n$  is a well-known polymer for many technological applications since it forms a film with high transparency, very good flexibility and wide commercial availability. Photosensitizable dyes incorporated in the PVA solid matrix have proved essential in the development of holographic and planar waveguides [4]. Dibbern *et al.* [5] had reported that the potential as probes for studying non-linear optical properties in devices is based on the property of dye molecules to exhibit a photobleaching reaction in polymer matrix. The MB dye doped in PVA forms a very attractive photosensitive material for non-linear applications such as holographic recording medium. It is also reported that methylene blue (MB) dye doped PVA without an electron donor did present photobleaching on the time scale of their investigation with irradiation intensity (He-Ne laser) used to obtain the photobleaching profiles.

### **EXPERIMENTAL PROCEDURE**

MB (BDH Chemicals Ltd. England) and polyvinyl alcohol (PVA)(Fluka Chemica) were used as received. The required amounts of PVA are dissolved in distilled water. A homogeneous solution with 8%(w/v) of PVA was obtained after the solutions were stirred continuously at room temperature for 6 hours. The methylene blue was then added to the PVA solution. Three different dye concentrations, namely  $6.3 \times 10^{-4}$  mol/l,  $1.9 \times 10^{-3}$  mol/l and  $3.1 \times 10^{-3}$  mol/l were prepared in this study. The MB doped PVA matrices were obtained by leaving the solutions in a flat bottom dish in the dark at room temperature for 48 hours. The sample was then kept in a dessicator under vacuum for another 24 hours. These samples were then cut into desired size for the following investigation. The optical absorption and transmission spectra of the MB sensitized PVA samples were recorded at room temperature using an uv-visible fibre optics spectrophotometer (OCEAN Optics, S2000), which was interfaced to a personal computer. The photochemical reaction of the sample occurred during uv-visible irradiation was monitored by collecting the absorbance and transmission data for 600s at intervals of 60s.

### RESULTS AND DISCUSSION

Fig.1 shows the recorded absorbance spectra of a pure PVA sample and the MB doped PVA samples at three different dye concentrations, namely  $6.3 \times 10^{-4}$  mol/l,  $1.9 \times 10^{-3}$  mol/l and  $3.1 \times 10^{-3}$  mol/l. From these spectra, the pure PVA solid matrix shows a lower absorbance with the value 0.04 throughout the wavelength region of 450nm-800nm. The excellent transparency of this polymer solid matrix is a very desirable feature for optical applications such as optical switching and optical memory storage system [4]. We also observed the absorption peak in MB doped PVA samples at dye concentrations of  $6.3 \times 10^{-4}$  mol/l,  $1.9 \times 10^{-3}$  mol/l and  $3.1 \times 10^{-3}$  mol/l are located at 660nm. This is the same to those reported previously [1,6]. Sergey *et al.* [6] had reported that the absorption peak at 660nm represents the transitions between the lowest excited singlet state and ground state of the MB dye molecules when irradiated with photon energy. The main absorption peak increases at higher concentration due to the increase in the number of dye molecules.

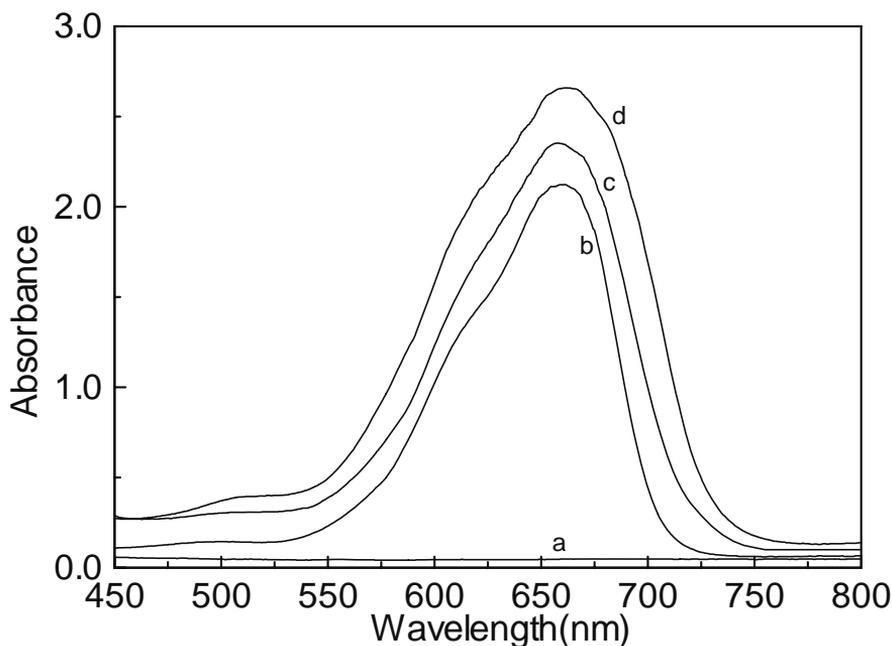


Fig. 1. The uv-visible absorption spectra of (a) a typical pure PVA sample and three different dye concentration of MB with (b)  $6.3 \times 10^{-4}$  mol/l ; (c)  $1.9 \times 10^{-3}$  mol/l and; (d)  $3.1 \times 10^{-3}$  mol/l.

The change of absorbance spectra observed during the continuous uv-visible irradiation of the MB doped PVA samples is shown in Fig.2. Fig.2(a) and Fig.2(b) represent the absorbance spectra at dye concentrations of  $3.1 \times 10^{-3}$  mol/l and  $6.3 \times 10^{-4}$  mol/l, respectively. We observed a stronger absorption region within the wavelength range of

550nm-720nm for the sample at dye concentration of  $3.1 \times 10^{-3}$  mol/l. The absorption peak located at 660nm decreases significantly with the increasing of irradiation time. The absorption peak became broadened and weaker and disappeared completely after 360s of irradiation. The decrease in absorbance indicates that continuous uv-visible irradiation causes the photoreduction of the colored MB dye molecules to leuco MB (colorless). It is clearly seen that the blue color of the MB doped PVA sample turned completely colorless after irradiation. Similar photodegradation process of MB was also observed in the sample with dye concentrations of  $3.1 \times 10^{-3}$  mol/l and  $1.9 \times 10^{-3}$  mol/l. The uv-visible sources having plenty of high-energy photons and bleaches the sample rapidly [4]. Thus, based on the observation in Fig. 2, we would say that the MB dye molecules embedded in PVA solid matrix exhibits an effective photobleaching process occurred. The experimental results obtained could be of use to the waveguide manufacture and holographic recording system [7].

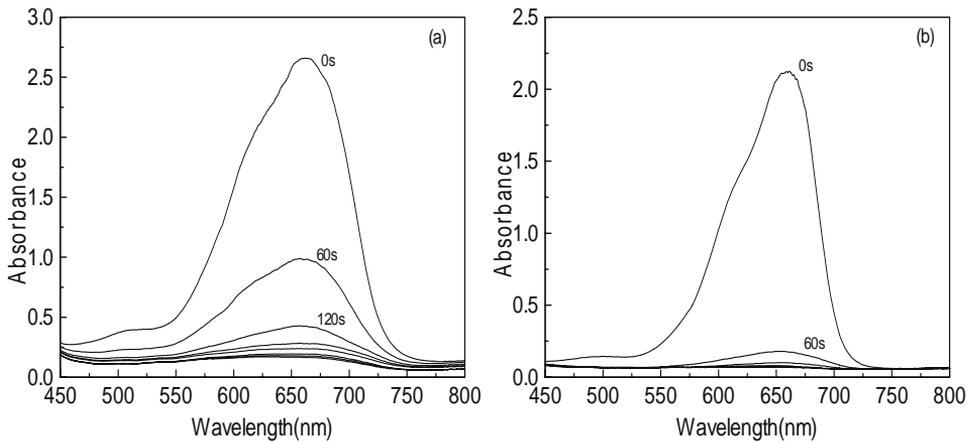
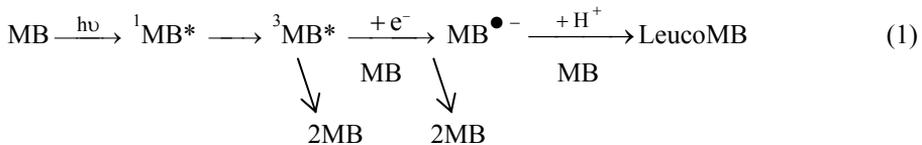


Fig.2: Variation in the optical absorption spectra with wavelength during uv-visible irradiation at dye concentrations of : (a)  $3.1 \times 10^{-3}$  mol/l ; (b)  $6.3 \times 10^{-4}$  mol/l.

Even though the exact mechanism responsible for photodegradation is not yet known, there are several possibilities for the photochemical reaction process. However, the photochemical reaction process takes place only when the dye molecules are in the excited state. In the present study, a proposed schematic representation of the reaction mechanism is summarized as follows [8-10]:



When the dye (MB) is irradiated with uv-visible light it passes to the first excited state ( ${}^1\text{MB}^*$ ) where it can change to triplet excited state with a longer lifetime ( ${}^3\text{MB}^*$ ). An electron is first transferred from the polymer matrix to the dye molecule producing the semireduced dye radical ( $\text{MB}^{\bullet-}$ ). The MB dye is then photoreduced by abstract of an

anion hydrogen from the PVA matrix, to produce the leuco form of the dye molecules (colorless MB). Talhavani *et al.* [4] had suggested that PVA itself is acting as an electron donor system and the production of the leuco form of the dye is a consequence of the electron-transfer process from the own polymer matrix, since no other electron donor additive was incorporated into the system. Therefore, this should be the most important contribution to the photodegradation process of MB sensitized PVA matrix. The excited MB dye molecules can also return to the electronic ground state by a deexcitation mechanism which is due to the dye-dye interaction between the excited dye molecules ( $^1\text{MB}^*$  and  $^3\text{MB}^*$ ) and the nonexcited dye molecule (MB).

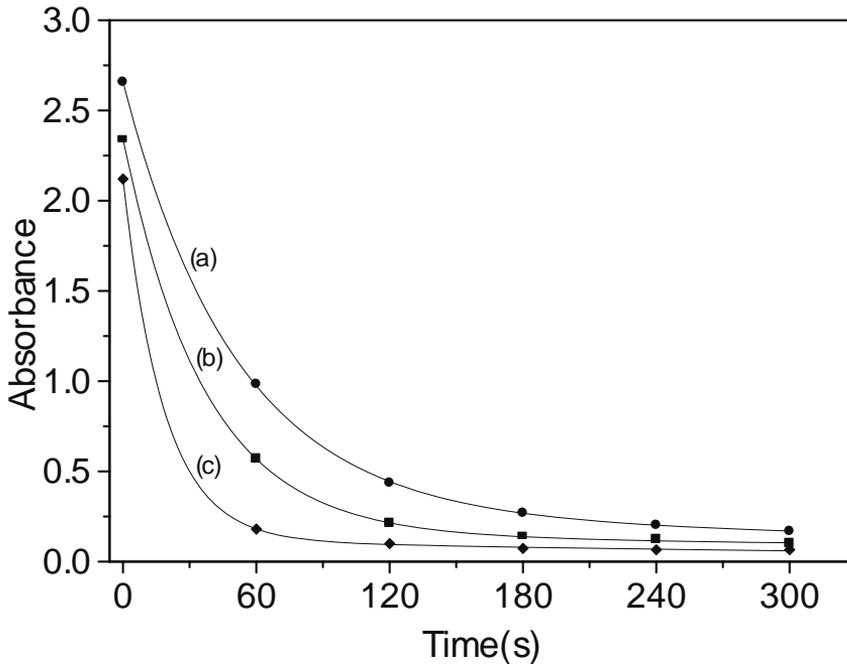


Fig.3. Plot of absorption peak versus irradiation time for three different dye concentration: (a)  $3.1 \times 10^{-3}$  mol/l ; (b)  $1.9 \times 10^{-3}$  mol/l and; (c)  $6.3 \times 10^{-4}$  mol/l.

From the spectra shown in Fig.2, there is a remarkable decrease in the absorbance of MB at lower concentration ( $6.3 \times 10^{-4}$  mol/l, Fig.2b) in comparison with that at higher concentration of MB ( $3.1 \times 10^{-3}$  mol/l, Fig.2a). The variation in the absorption peak (660nm) as a function of irradiation time at three different dye concentrations is shown in Fig. 3. In the present work, the color change of the irradiated samples could be calculated by the percent colour bleaching (% of bleaching) using the following relationships [11]:

$$\% \text{ of bleaching} = \frac{A_0 - A_t}{A_0} \times 100\% \quad (2)$$

where  $A_0$  is the absorbance in the beginning of irradiation and  $A_t$  is the absorbance after irradiation at time  $t$ . In the present work, after the irradiation for the first 60s, the % of bleaching of each sample at dye concentration of  $6.3 \times 10^{-4}$  mol/l,  $1.9 \times 10^{-3}$  mol/l and  $3.1 \times 10^{-3}$  mol/l are 92%, 76% and 63%, respectively. This indicates that the sample with lower MB concentration bleached much faster compared to that at higher concentration. It is also suggested that for achieving faster photobleaching at higher concentration, higher exposure energy is needed. Cristina *et al.* [8] had reported that by increasing the concentration of dye molecules, the possibility of the dye-dye interactions between the excited dye molecule ( $^3\text{MB}^*$  and  $^1\text{MB}^*$ ) and the nonexcited dye molecule (MB) are increased and produces the non-bleached molecules in the electronic ground state. This leads to the faster photobleaching process at lower concentration of MB dye molecules.

We have also observed that the bleached PVA sample was recovered to its original colour after being exposed to atmospheric air in the dark for 12 hours. This phenomenon was confirmed by the recovery of the absorbance peak as shown in Fig.4. This effect is due to the reoxidation of the leuco form of the dye molecules as given by:



This observation implies that the leuco form of the dye molecules can return to the ground state if it is in contact with atmospheric oxygen [7].

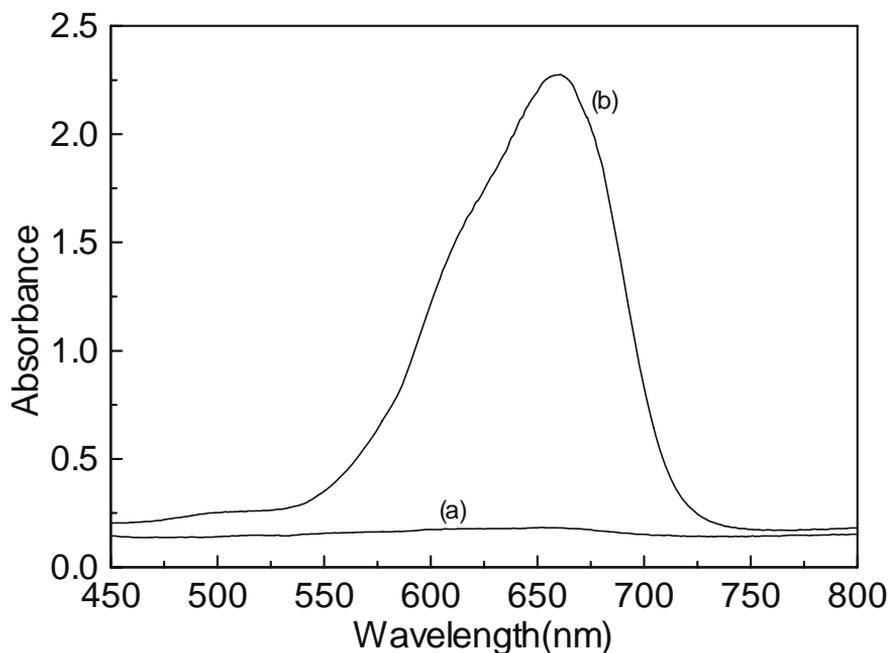


Fig. 4. Absorbance spectra for the PVA doped with  $1.9 \times 10^{-3}$  mol/l : (a) after exposed to uv-visible radiation (b) after being exposed to atmospheric air for 12 hours.

## CONCLUSION

In this paper, an uv-visible fibre optics spectrophotometer has been used to investigate the photobleaching process of the MB dye molecules embedded in the solid matrix poly(vinyl alcohol) PVA. The absorbance peak of the sample centered at 660nm decayed significantly with time during continuous uv-visible light exposure. On illumination the excited dye molecule changes its structure giving a colorless molecule. We also found that a faster photobleaching process was occurred at lower dye concentration compared to that at higher concentration. Hence, it is evident that the MB molecules are undergoing some change of state which changes its absorption properties, and for more molecules (higher concentration) it may need longer exposure time for the MB dye molecules to change to the leuco form of MB. The recovery of the photobleached sample was also observed after keeping the sample 12 hours in the dark.

## ACKNOWLEDGEMENT

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