

Radiation Induced Decoloration of Reactive Dye in PVA Films for Film Dosimetry

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Abstract: The investigation of film dosimeters made from polyvinyl alcohol (PVA) films dyed with methyl orange (MO) to enable their use in high dose radiation processing applications was studied. The dosimetric change in these films at pre and post irradiation was studied spectrophotometrically. Radiolytic bleaching was observed in PVA aided films exposed with Cs¹³⁷ γ -source in dose range of 100-200kGy. The effects of pH, dye concentration and film thickness on the radiation response of the film dosimeters were discussed. The stability of MO-PVA films before and after exposure of radiation was also examined at ambient temperature and was found to be higher for long times at pre and post irradiation stages.

Keywords: Thin film, polyvinyl alcohol, methyl orange, γ -radiation, decoloration.

INTRODUCTION

Radiation indicators based on their radiation-induced color change have long been used for identification of irradiated and unirradiated products in radiation sterilization and food irradiation. Due to their sensitivity towards various influence factors (dose rate, light, humidity, temperature etc.) these are used for quantitative purposes [1]. A number of chemical and physical changes are caused in the exposed material by ionizing radiations [2-5]. The scientific foundation of the radiation technology is an extensive knowledge of chemical, biological and physical effects of radiation on materials [5]. Thermal transport of complex liquid materials is a significant parameter being used in the heat design process [6, 7], and dosimetry plays an important role in the quality control of radiation processing in material industry [8]. The irradiation processing is being used for several purposes, such as food irradiation, sterilization of surgical equipments, polymerization and cross-linking of polymers [9]. Therefore, thin film dosimeters are of interest for use in radiation processing because of their convenient characteristics [10]. Polymeric films are lightweight and portable detectors and can be easily put at any location. These films because of their ruggedness, long shelf-life stability, ease of handling and convenient spectrophotometric analysis are usually made available in large reproducible batches [9, 11].

The current work deals with investigation of film dosimeters made from PVA dyed with methyl orange (MO) to enable their use in high dose radiation processing applications. The films were irradiated with Cs¹³⁷ gamma source. The effects of pH, dye concentration and film thickness on the radiation response of the film dosimeters were discussed.

MATERIALS AND METHODS

The MO-PVA radiochromic dye films were prepared by using polyvinyl alcohol powder (PVA) (VWR scientific) containing indicator, i.e., methyl orange (C₁₄H₁₄N₃NaO₃S, MW: 327.33). The molecular structure of MO is shown in Figure 1. Three grams of PVA powder was dissolved in 50 ml doubly distilled water to prepare a stock gel polymer solution. The well stirred polymer solution was kept at 45°C for about 4hrs to dissolve the compound powder completely and then left to be cooled. Indicator of different concentration such as C₁=0.2gm/L, C₂=0.4gm/L and C₃=0.6gm/L was added to the polymeric gel solution and kept well stirred for 1hr at room temperature to get a uniform dye solution. The natural pH of the aqueous solution was 6.5. The sample solutions of two different chemical nature, i.e., Acidic and Alkaline solutions, were prepared. The pH of the samples was set by using 1 Molar solution of hydrochloric acid (HCl) and sodium hydroxide (NaOH), respectively. The thin films were made by pouring the dyed solution on a commercial glass plate and allowed drying for 24h at room temperature. Each sample was sealed into a small dark plastic pouch and stored under laboratory

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conditions. The thickness of each film was found to be 0.033 ± 0.003 mm.

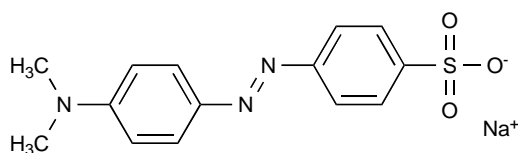


Figure 1: Molecular structure of Methyl Orange (MO).

Cs^{137} γ -source from Nuclear Institute of Agriculture and Biology (NIAB), Faisalabad, Pakistan having dose rate 660Gy/hour was used for irradiation at constant temperature. The samples were irradiated within the dose range 100-200kGy. The UV/VIS spectrophotometer (Perkin Elmer Precisely Lambda 25 UV/VIS) was used to measure the optical absorption spectra of the unirradiated and irradiated films. The film thickness was measured using an electronic digital micrometer with the precision of $\pm 1 \mu\text{m}$. The pH of the solutions was determined by pH meter (3510 pH meter (Jenway)).

RESULTS AND DISCUSSION

Absorption spectra

The optical absorption spectra of unirradiated and irradiated films were measured in the wavelength range of 300-800nm using a UV/VIS spectrophotometer. The absorption spectra of these unirradiated films show a main absorption band in the visible region peaking at 488nm (λ_{max}) for MO-PVA as shown in the Figure 2.

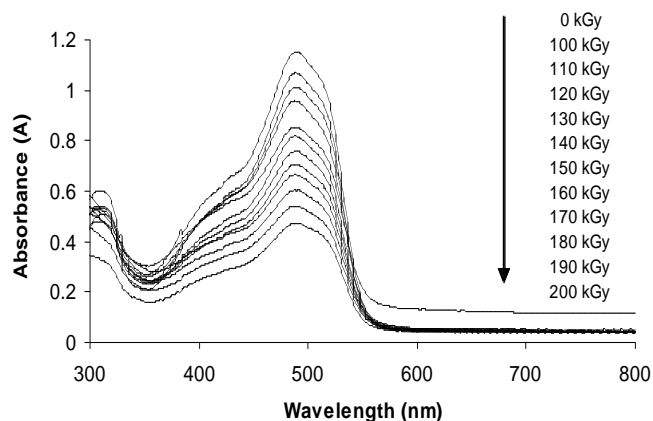


Figure 2: Absorption spectra of unirradiated and irradiated MO-PVA films to different absorbed doses.

The amplitude of these absorption bands decreased gradually with the increase of dose of γ -rays without changing λ_{max} . Absorption spectra of undyed PVA film were shown in Figure 3. When undyed PVA film was irradiated to dose higher than 150kGy, this produced

pale brownish coloration and, therefore, can be served as a color indicator.

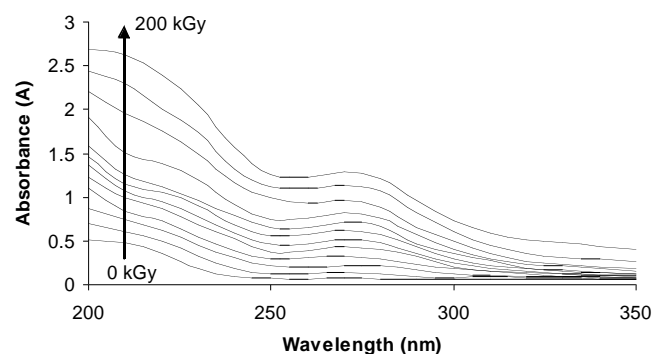


Figure 3: Absorption spectra of undyed PVA films irradiated to different absorbed doses.

Irradiation of Films

It was noticed that the color of films changed after irradiation with γ -rays. The color of MO-PVA changed from orange to colorless. Under γ -irradiation, hydrogen radicals liberated from PVA, may reduce the azo group i.e., $-\text{N}=\text{N}-$ of methyl orange resulting in the disappearance of the chromophore. Hence, the film becomes colorless as Figure 4 depicts.

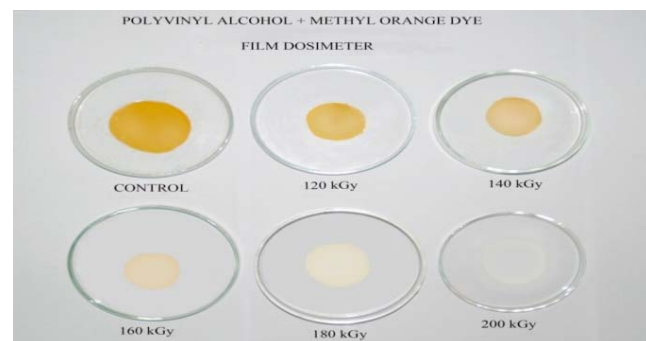


Figure 4: PVA films of methyl orange irradiated to different absorbed doses.

Response Curves

Figure 5 shows the dose response curves of the films in terms of change in optical density at λ_{max} per unit thickness, $\Delta A/d$ (mm^{-1}) against absorbed dose; where, d =film thickness and $\Delta A=A_0-A_i$, giving A_0 and A_i as values of optical absorbance at λ_{max} of unirradiated and irradiated films respectively. Linear relationship was obtained for films of MO-PVA throughout absorbed dose range up to 200kGy.

Effect of Concentration

The effect of dye concentration on the response of the dosimeter film, made of PVA solutions containing

different concentration of MO such as $C_1=0.2\text{gm/L}$, $C_2=0.4\text{gm/L}$ and $C_3=0.6\text{gm/L}$, was investigated. Figure 6 clarifies that specific absorbance increased with the increase of dye concentration.

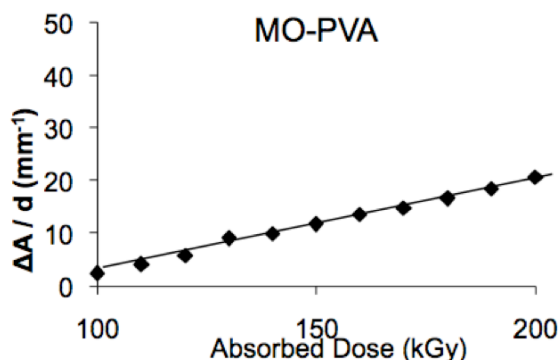


Figure 5: Dose-response curves of MO-PVA at λ_{max} 488nm.

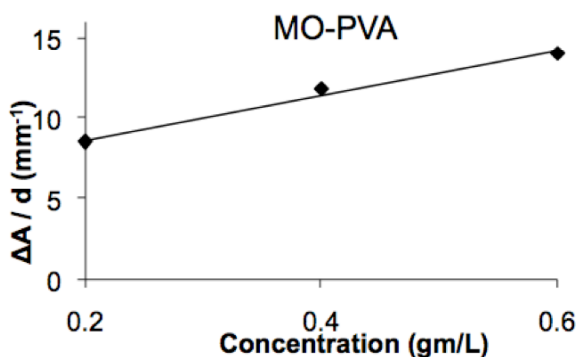


Figure 6: Effect of concentration of dyes on the response ($\Delta A/d$) of dyed PVA films of MO-PVA at λ_{max} 488nm.

Effect of pH

To study the effect of pH on the response of the dosimeter film acidic (having pH value 2, 4 and 6) and alkaline (having pH value 8, 10 and 12) aqueous solutions were prepared to make the dosimeter films. Figure 7 shows that higher sensitivity was observed in the case of the films made from alkaline films.

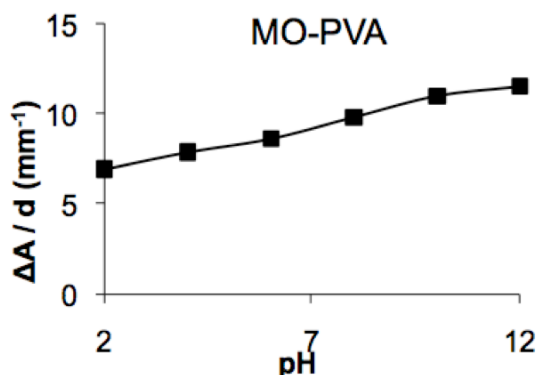


Figure 7: Effect of pH on the response ($\Delta A/d$) of dyed PVA films of MO-PVA at λ_{max} 488nm.

Effect of Thickness

The effect of the film thickness on the response of the dosimeter film was investigated by preparing films of different thickness (0.017, 0.033 & 0.04 mm). It can be seen that with the increase of film thickness, specific absorbance also increases (Figure 8).

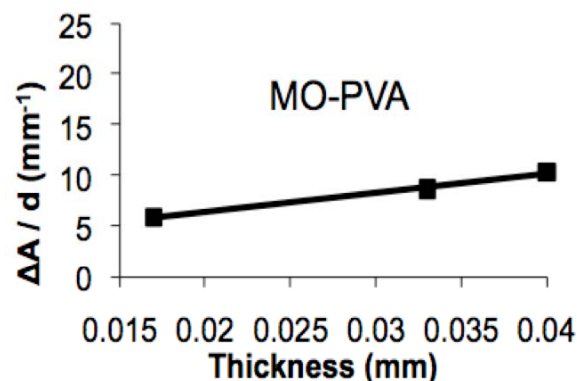


Figure 8: Effect of film thickness on the response ($\Delta A/d$) of dyed PVA films of MO-PVA at λ_{max} 488nm.

Pre-Irradiation Stability (Shelf Life)

Stability measurements before irradiation of the dyed films were made by storing films in darkness and light at ambient temperature. In addition, the films were read spectrophotometrically at different times during the pre-irradiation storage period of 30 days as shown in Figure 9. It can be seen that the MO-PVA film exhibited excellent stability before irradiation.

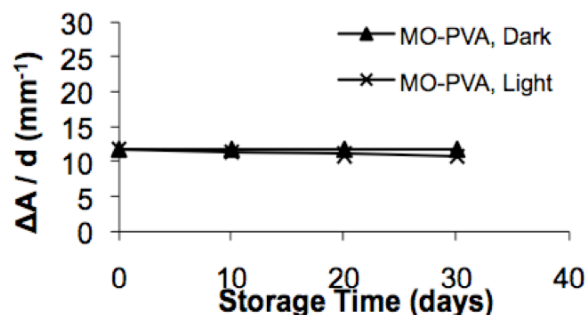


Figure 9: Absorbance values of unirradiated films as a function of time under the storage for 30 days.

Post-Irradiation Stability

The post-irradiation stability is investigated by storing films in the dark and under laboratory fluorescent lights at room temperature as shown in Figure 10. It can be seen that the irradiated films had a good stability in darkness, the film containing MO showed excellent stability in light with less than 3% increase in absorbance noticed.

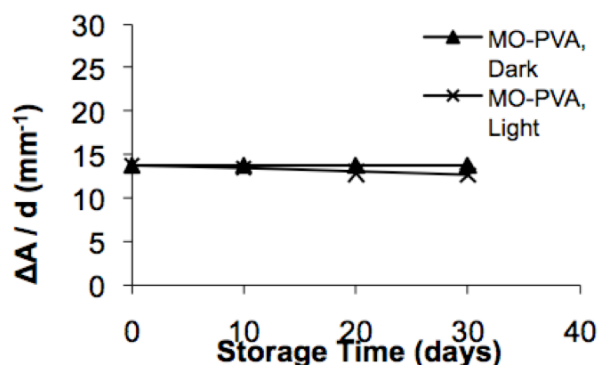


Figure 10: Absorbance values of irradiated films as a function of time under the storage for 30 days.

CONCLUSION

The preliminary study on the PVA based films containing methyl orange dye indicates that radiation induced decoloration of these films can be used for dosimetry. The results indicate that the response of these films depends on the absorbed dose, dye concentration, pH and film thickness. The MO-PVA film is highly stable for long times before and after irradiation. PVA based films are easy to make and do not require toxic solvents in the preparation therefore, these are amenable for large-scale production and application for routine irradiation processes of medical equipments.

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