To Determine Dose Response Curves of Dyed Polyvinyl Alcohol Films Irradiated with Gamma-Rays

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Abstract

The Polyvinyl Alcohol (PVA) films dyed with different colors such as methylene blue (MB), methyl orange (MO), methyl red (MR) and crystal violet (CV) were investigated. The dyed PVA films were irradiated by with Co^{60} γ-source in dose range of 1 - 150 kGy. The optical density change in these films at pre and post irradiation was studied by spectrophotometer. The gamma dose response curves of the dyed PVA films were described by saturated exponential function of the energy transfer model with high correlative coefficient. The color sensitivities on the dyed PVA films irradiated by source were different. The PVA films dyed with MB had the highest sensitivity.

Keywords

Dyed Thin Film, Dose Response Curves, Optical Density, Methylene Blue, Methyl Orange, Methyl Red and Crystal Violet

1. Introduction

PVA is an excellent matrix for radiochromic centres and widely used for low- and high-dose dosimetry purposes. For example, the colored polyvinyl alcohol films can be used in dosimetry for gamma rays and neutrons in nuclear reactors [1]. Using dosimeters for high doses control of radiation processing is extremely important in the field of radiation technology. The PVA is a tissue-equivalent organic material that occupies a very small place in space. So the PVA material is highly suitable to use in gamma dose measurements [2] [3] [4] [5] [6]. Some researchers in the world have used different colors which have radiation sensitive properties to add to the PVA films for high dose control. The dyed PVA film containing a mixing of ethyl violet and bromophenol blue [7], and the dyed PVA

film containing methyl red [8] are useful as routine high-dose dosimeter with Co^{60} γ-source in the 1 - 30 kGy range. The film dosimeters made from PVA films dyed with methylene blue [9] and methyl orange [10] were studied for high-dose control with Cs^{137} γ-source in dose range of 100 - 200 kGy.

Most of these studies have carefully surveyed the factors that affect the discoloration of films such as pH, color concentration, film thickness, pre-irradiation and post-irradiation stabilities. Apart from that, the researchers usually pay attention to investigate discoloration of post-irradiation films for different dose ranges [7] [8] [9] [10]. However, they did not clearly define the dose response curves for the different dose ranges that they surveyed.

The current works are to define the dose response curves of the dyed PVA films. Several dyed PVA films containing difference colors such as crystal violet, methyl red, methylence blue and methyl orange were strongly changing the original colors under Co^{60} γ-source and became stable radiochromic thin films which can be used as dosimeter for measurement of radiation doses in different dose ranges.

2. Materials and Methods

We prepared four types of film with four different colors. They were the CV-PVA dyed films containing 1 mL crystal violet 2×10^{-3}M ($C_{25}H_{30}ClN_3$, Mw = 407.98), the MR-PVA dyed films containing 1 mL methyl red 0.4×10^{-3}M ($C_{15}H_{15}N_3O_2$, Mw = 269), the MB-PVA dyed films containing 5 mL methylene blue 10^{-3} M ($C_{16}H_{18}ClN_3S_x \times H_2O$, Mw = 391.86) and the MO-PVA dyed films containing 0.2 mL methyl orange 10^{-3} M ($C_{14}H_{14}N_3NaO_3S$, Mw = 327.34). PVA from SIGMA Mw = 89,000 - 98,000 g/mol, 99% hydrolyzed, was used as received. The molecular structures of indicators are shown in Figure 1.

Two grams of PVA power was dissolved in 50 ml of de-ionized distilled water
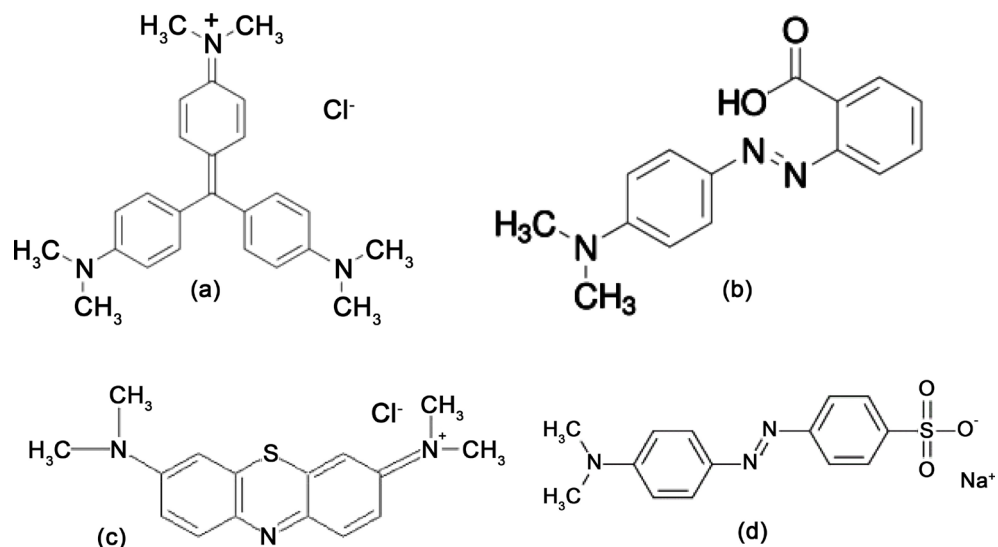

Figure 1. The molecular structures of crystal violet (a), methyl red (b), methylene blue (c) and methyl orange (d).

by heating up to 60°C and stirred for homogeneous solution (magnetic heater). PVA solution changed transpicuous color was added 1 mL crystal violet 2×10^{-3} M and further stirred for half an hour so as to obtain a colored PVA solution uniformly. Films of this solution were prepared by pouring it on a flat glass plate when temperature of solution was from 45°C to 50°C. The dyed PVA films would dry naturally within 72 hours at room temperature. CV-PVA film was peeled off the glass plate and cut into thin films of 0.8 cm × 4 cm. Each sample was sealed into a dark plastic pouch and stored in desiccator at laboratory conditions.

The MR-PVA dyed films, the MB-PVA dyed films and the MO-PVA dyed films were prepared same the CV-PVA dyed films.

Co^{60} γ-source from Hanoi Irradiation Center, Vietnam Atomic Energy Institute have 4.07×10^{15} Bq radioactive activity. The samples were irradiated with the dose range 1 - 150 kGy at temperature 23°C. The UV-VIS 2450 spectrophotometer was used to measure the optical absorption spectra of the unirradiated films and irradiated films.

From the results of optical density values on the pre and post-irradiation films, we determined the gamma dose response curves and investigated the different color sensitivity of four film types with four different colors.

3. Results and Discussion

3.1. Absorption Spectra

The optical absorption spectra of unirradiated and irradiated films were measured in the wavelength range of 540 - 660 nm and maximum at 599 nm with CV-PVA, 400 - 600 nm and maximum at 520 nm with MR-PVA, 500 - 750 nm and maximum at 668 nm MB-PVA and 300 - 600 nm and maximum at 440 nm with MO-PVA as shown in the Figures 2-5. The colors for films of CV-PVA
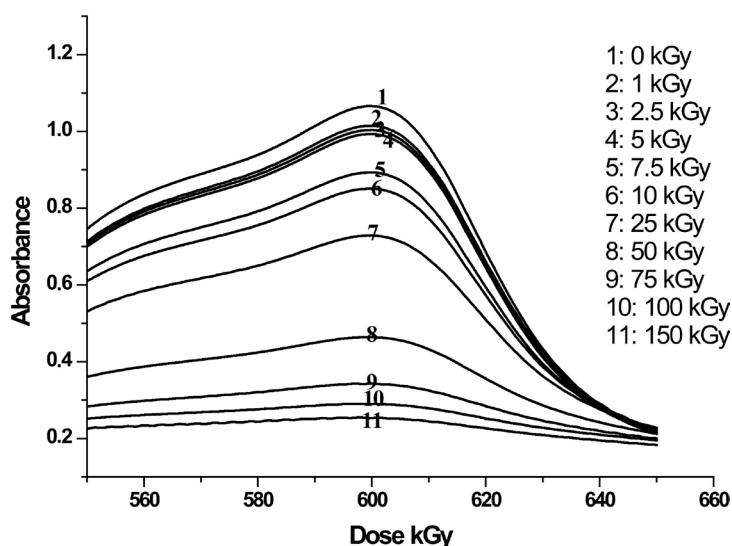
Figure 2. The absorption spectra of unirradiated and irradiated CV-PVA films measured at wavelength range 540 - 650 nm for difference doses.
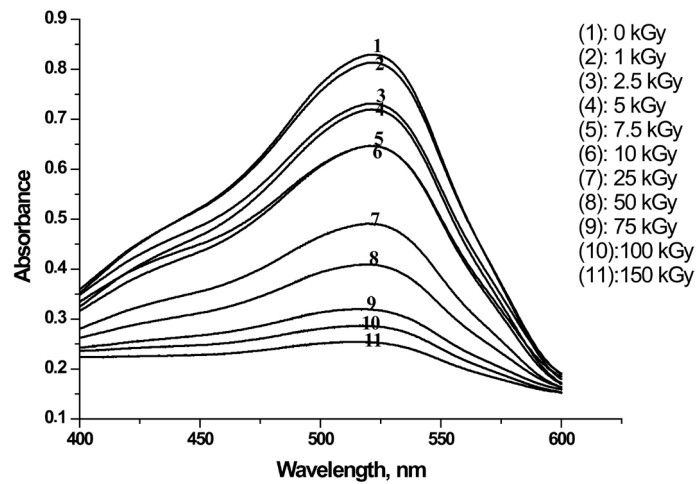
Figure 3. The absorption spectra of unirradiated and irradiated MR-PVA films measured at wavelength range 400 - 600 nm for difference doses.
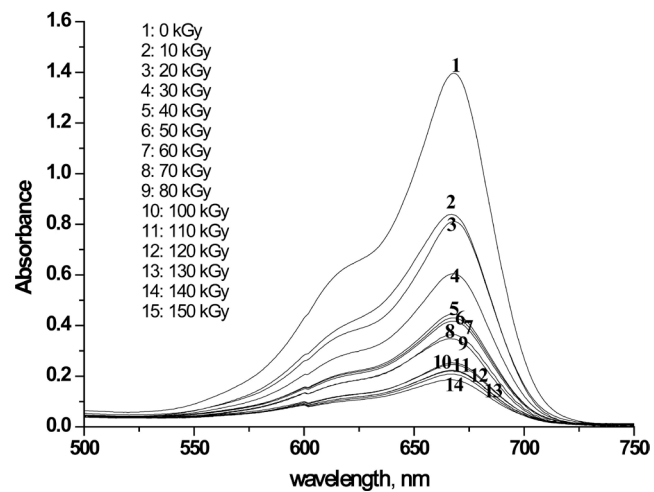

Figure 4. The absorption spectra of unirradiated and irradiated MB-PVA films measured at wavelength range 500 - 750 nm for difference doses.
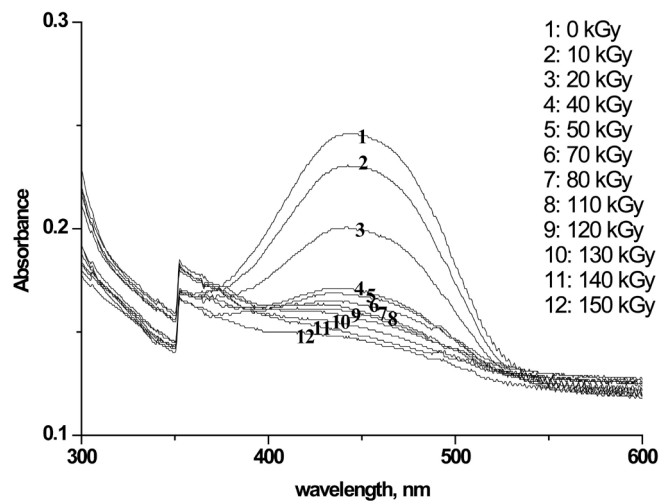

Figure 5. The absorption spectra of unirradiated and irradiated MO-PVA films measured at wavelength range 300 - 600 nm for difference doses.

changed from dark purple to light purple, MR-PVA changed from dark pink to light pink, MB-PVA changed from dark blue to light blue and MO-PVA changed from yellow to light pink.

The amplitude of these absorption bands decreased gradually with the increase of dose of γ-ray without changing $\lambda_{\max}$. The change in optical density at $\lambda_{\max}$ per unit thickness increased when γ-ray dose increased.

3.2. Response Curves

The response curves have been built by characteristic functions of radioactive energy transfer from γ-source to material made dosimeters. The energy transfer process is mainly performed by δ-electrons. They get enough energy and leave their orbits in the atom to become free electrons. According to the energy transfer model, the response curves of the dyed PVA films can be expressed as the saturated exponential function of the optical density values n(D) as follows:

$$n(D) = n_s \left[1 - e^{-kD} \right] + n_o e^{-kD} \tag{1}$$

where D is dose; n_0 and n_s are respectively number of the activated element at $D = 0$ and $D = \infty$; k is the total probability that one radiation sensitive element of the system will be activated per unit of time. In fact, k consists of two components:

$$k = p + q \tag{2}$$

where p is the probability that one sensitive element will be activated per unit of time; q is the probability that one activated element experiences reactivation per unit of time [11] [12].

Optical densities of the dyed PVA films decreased when they irradiated gamma source with increasing dose. The absorbance reductions of films were fitted in formula (1) giving the response curves (as the dose characteristic function) which depicted in Figure 6 and Table 1.
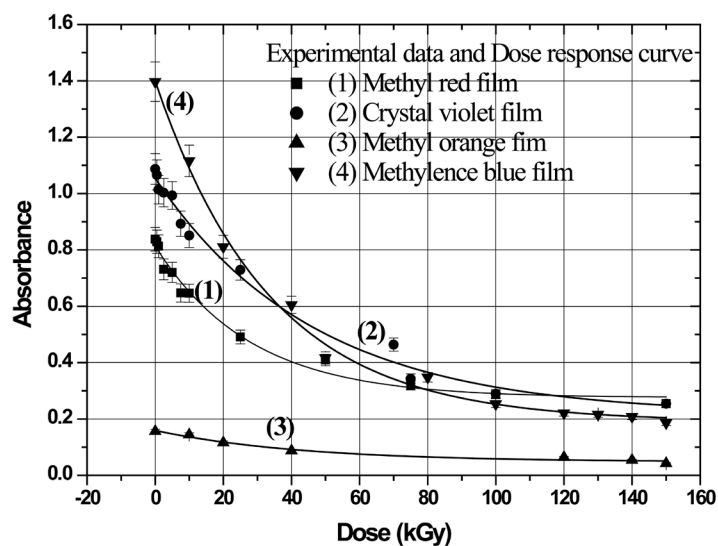

Figure 6. The response curves of the dyed PVA films.

Table 1. The coefficients of the gamma dose response curves.

Dyed film	n_o	n_s	n_o/n_s	k	R^2
Methyl red	0.814 ± 0.011	0.276 ± 0.021	2.955 ± 0.227	0.036 ± 0.005	0.98664
Crystal violet	1.052 ± 0.014	0.214 ± 0.030	4.909 ± 0.689	0.023 ± 0.005	0.99426
Methyl orange	0.159 ± 0.007	0.051 ± 0.006	3.100 ± 0.404	0.024 ± 0.005	0.96574
Melthylene blue	1.399 ± 0.031	0.190 ± 0.020	7.352 ± 0.788	0.030 ± 0.002	0.99435

Thus, the gamma dose response curves of the dyed PVA films determined by saturated exponential function of the energy transfer model are perfectly consistent with the high correlation coefficient between theory and experiment.

3.3. Sensitivity of the Dyed PVA Films

To assess the color variability of the dyed PVA films which were irradiated by the gamma source, we determined the color sensitivity of a dosimeter by the formula:

$$s = \frac{n_0}{n_s} \tag{3}$$

where n_0 and n_s are respectively number of the activated element at $D = 0$ and $D = \infty$. From expression (3) it is clear that s value (the color sensitivity) is big, the discolorment of the film is big. The sensitivities of different dyed films were shown in Table 1. These results showed that The MB-PVA dyed films were the best dosimeters, while MR-PVA dyed films were the bad dosimeters.

4. Conclusion

Study on the optical density change of the dyed PVA films at pre and post irradiation by Cs^{137} γ-source in dose range of 1 - 150 kGy shows that the γ-ray absorptions of these films were described by saturated exponential function of the energy transfer model. They are appropriate to make dosimeters for routine irradiation processes. The sensitivity results indicate that the MB-PVA dyed films are the best dosimeter.

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