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# THE EFFECTS OF RADIATION ON OPTICAL PROPERTIES OF DYED POLY (VINYL ALCOHOL) BLENDS

E.B. Saion*, Susilawati * [1], A. Doyan* [1], W.M.Daud *, M.Zaki.A. Rahman**, K.Z.M. Dahlan[#] and T. Kadni[#].

* *Department of Physics, Universiti Putra Malaysia, Serdang, Malaysia.*
*Tel: 03-89466654; Fax: 03-89454454.*

*** Department of Chemistry, Universiti Putra Malaysia, Serdang, Malaysia.*

[#] *Malaysian Institute for Nuclear Technology Research (MINT), Bangi, Malaysia*
[1] *Department of Physics, Universitas Mataram, Lombok, NTB, Indonesia.*

*Email: elias@fsas.upm.edu.my*

## ABSTRACT

The effects of gamma irradiation on the optical properties of dyed poly vinyl alcohol (PVA) films containing trichloroaceticacid (TCA) and acid-sensitive cresol-red dye have been studied. These polymers were exposed to different gamma doses in the range from 1 to 12 kGy. These polymer undergo color change from purple (color of base form) to yellow (color of acid form) upon exposure to gamma irradiation. The radiation-induced change in color was analyzed using UV-Vis spectrometer in the range 350 – 650 nm. The absorbances of polymer in the visible range have been studied in order to develop a dosimeter for gamma ray dosimetry. The absorption spectra produced two absorption bands, peaking at 575 nm for low doses and 438 nm for high doses. The dose-response was plotted by the change in absorbance as a function of absorbed dose. Results of the dose-response curves show the absorption decreases and increases exponentially at bands 575 nm and 438 nm respectively.

## INTRODUCTION

Interest in food irradiation technology for preservation of food and improving hygienic quality of food is increasing worldwide and in some countries commercialisation of food irradiation has already become a reality. A reliable dosimetry system is necessary for commercialisation of food irradiation to satisfy regulatory requirements and for quality assurance [1].

For routine dose monitoring in radiation processing the polymeric dyed flexible films are considered to be the most common ones as dosimeters, dose labels and indicators [2]. Polymeric films dosimeters are the most commonly used indicators and monitors of absorbed dose for routine use in radiation processing by electron beams and gamma rays. Many dyed poly (vinyl alcohol) films have been developed and investigated for the possibility of their being used to measure neutron doses in nuclear reactors and doses of X- rays, γ-rays, and electron beams. All these dyed PVA systems are bleached by irradiation, the extent being to which the colour change is used for determining the absorbed dose [3]. A new radiation sensitive indicator consisting of a poly (vinyl alcohol) film containing pH indicating dye and water-soluble chlorine containing substance has been developed by Abdel-Fattah, et al, (1996). The chlorine containing polymers is dehydrochlorinated when the material is irradiated, thereby decreasing the pH and causing the acid sensitive dye to change colour [4].

Acid - base indicators are usually organic compounds, which change colour in relation to the concentration of hydrogen ions. The change in colour is based on absorption of release of protons. During this, the delocalizing capacity or mesomeric distribution of the TL electron system is changed. One of the properties of acid - base indicators is that they do not change colour exactly at one pH value, but within a wide pH range. The transition point of an acid - base indicators is defined as the point at which the acid and alkaline forms of the acid - base indicators. Acid-base indicators can exist in equilibrium between two tautomeric forms having different colours and the ratio of the two forms depends on the concentration of hydrogen ion in the medium [5]. In our case, cresol red (CR) is yellow at $2.8 < pH > 7.2$, red at $pH < 2.8$ and purple at $pH > 8.8$.

In a previous paper have been reports of cresol-red dyed PVA films containing chloral hydrate which undergo colour change from yellow to red after radiation [6]. In this article, we report the characteristics of cresol-red dyed PVA films containing TCA (trichloroaceticacid), which undergo colour change from purple (the alkaline form of the dye) to yellow (the acidic form of the dye) for low absorbed doses.

## MATERIAL AND METHODS

The stock solution of cresol red dye was prepared by dissolving 0.08 g of cresol-red indicator (product of fisher Chemical UK) in 15 ml of aqueous NaOH solution ([NaOH] = 0.1 mol/1) and then the volume was completed by ethanol in a 50 ml volumetric flask. PVA from SIGMA Mw = 70,000 g/mol, 99 – 100% hydrolyzed, was used as received.

PVA solutions were made by dissolving PVA powder in double distilled water at about 90 $^{o}$C. The solution was stirred throughout at that temperature for 2 hours and then left to cool. A 1-ml of the indicator stock solution was added and kept well stirred at room temperature for about 2 hours in order to obtain a uniformly dyed solution. To each 50 ml of the well-mixed solution, 20 – 35% of TCA were added, stirred and poured onto a 15 x 15 cm horizontal glass plate and dried at room temperature for about 72 hours. After drying, the films were peeled off and cut into 2 x 4 cm pieces, stored and ready for irradiation. The average thickness of the film was found to be 70 μm.

The absorption spectra of the unirradiated and irradiated film dosimeters were measured using UV-Visible spectrometer (Shimadzu, Model 1601) in the wavelength range 350 - 650 nm.

The film irradiations were carried out in the $^{60}$Co γ-rays chamber at the Malaysian Institute for Nuclear Technology Research (MINT) at Bangi. The absorbed dose rate was calibrated using Fricke dosimetry method to be 9.39-kGy/h. For each dose the film samples of different TCA concentrations were placed simultaneously at the centre of the chamber surrounded with polystyrene for radiation equilibrium purposes. Film samples for every TCA concentrations were exposed at different absorbed dose ranging from 0 kGy to 12 kGy. All irradiations were conducted at room temperature throughout this work.

## RESULTS AND DISCUSSIONS

Absorption spectra of unirradiated and irradiated dosimeters containing 20 % of TCA at different absorbed doses are shown in Fig. 1. The spectra produce two absorption bands in the visible region, peaking at 575 nm for low doses and 438 nm for high doses.

The absorbance of unirradiated dosimeter at absorption band 575 nm this band is the characteristic of the purple colour. The absorbance of irradiated dosimeters decreases gradually with an increase of the absorbed dose. As the dose increases, hydrogen and chlorine ions of TCA break from the carbon and radiation-induced free radicals are then combined to the formation of acid, which lowers the pH of the dosimeters. Fig. 2 shows the absorbance at absorption bands of 575 nm and 438 nm for the dosimeter containing 20 % of TCA. The point at which two curves are crossing may be use to estimate the minimum dose at which the dosimeter starts to change its colour from purple to yellow. Fig. 3 shows the minimum doses at which the dosimeters of different concentrations of TCA start to change colour.

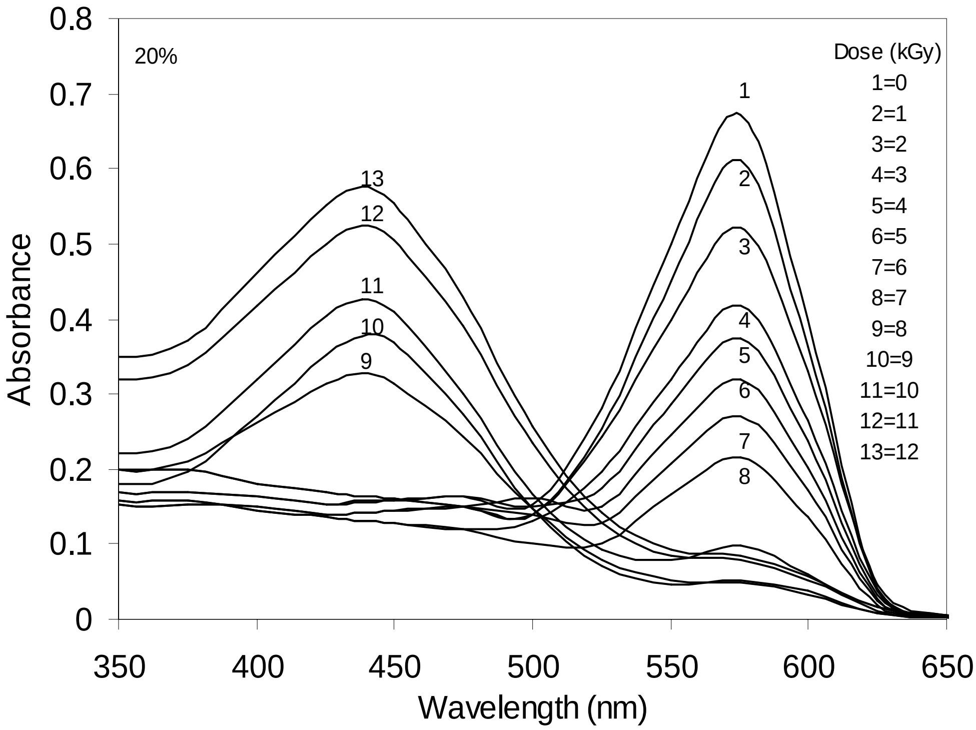


Fig.1: Absorption spectra of PVA film dosimeters containing 20 % of TCA irradiated at different absorbed doses.

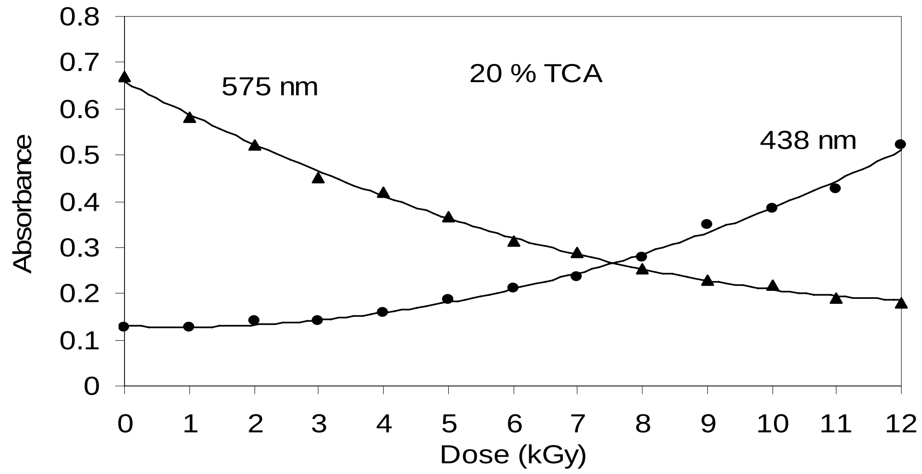


Fig. 2: Absorbance at 575 nm and 438 nm absorption bands for dosimeter containing 20 % of TCA.

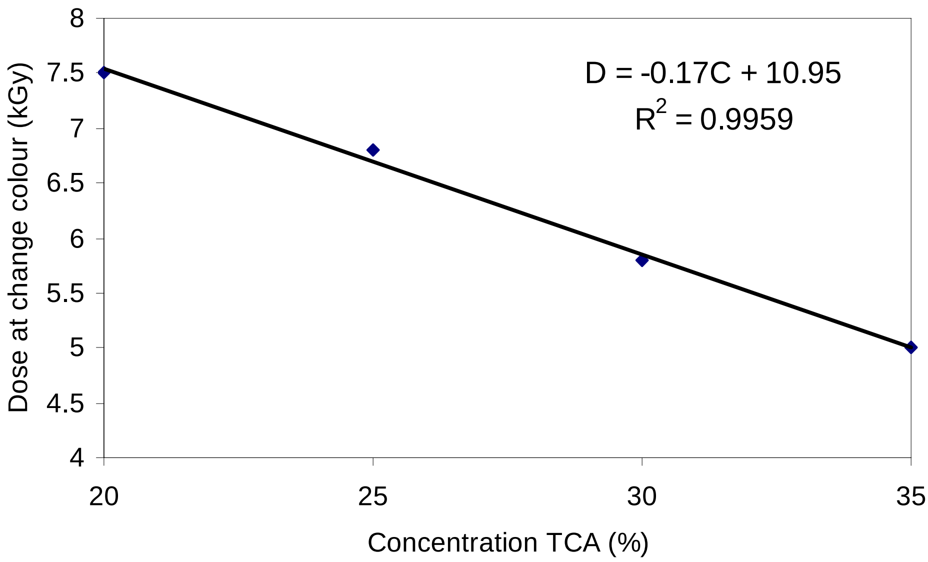


Fig. 3: Minimum doses estimated for the dosimeters to change colour from purple to yellow.

The dose-response of the unirradiated and irradiated PVA dosimeters containing different concentrations of TCA have been analysed in terms of the change in the absorbance normalized per unit film thickness as a function of absorbed dose. Fig. 4 and Fig. 5 show the characteristics of the dose-response curves for absorption bands at 575 nm and 438 nm respectively. The S-shape is a well-known characteristic of radiation response by acid-base pH indicators. The dose-response curves of absorption band at 438 nm increase exponentially and may be fitted to equation $y = y_0 e^{D/D_0}$. However, the dose-response curves of absorption band at 575 nm decrease exponentially and may be fitted to equation $y = y_0 e^{-D/D_0}$. The results of the fitting are shown in Fig. 6 and 7. The dose sensitivity parameter $D_0$ at 575 nm and 438 nm increases with concentration of TCA increase.

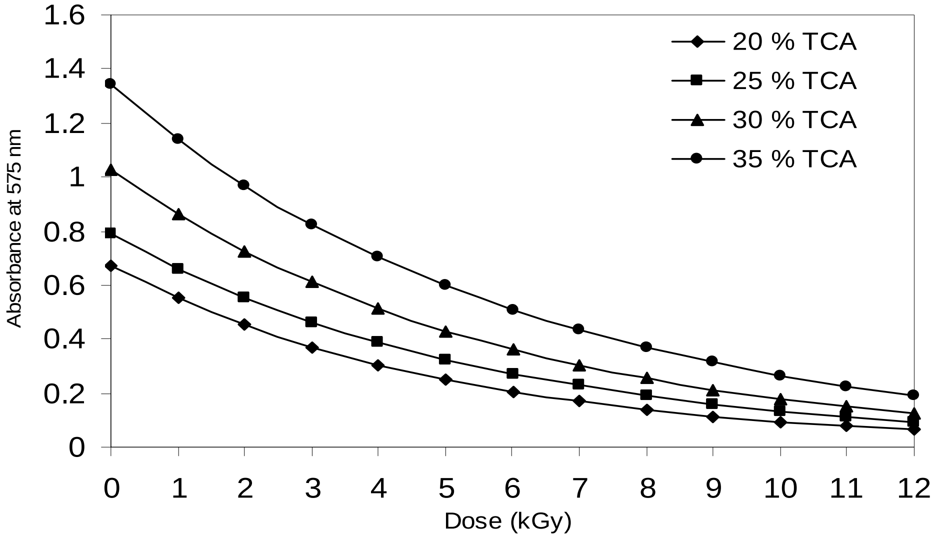


Fig. 4: Dose-response curves of PVA films for absorption band at 575 nm.

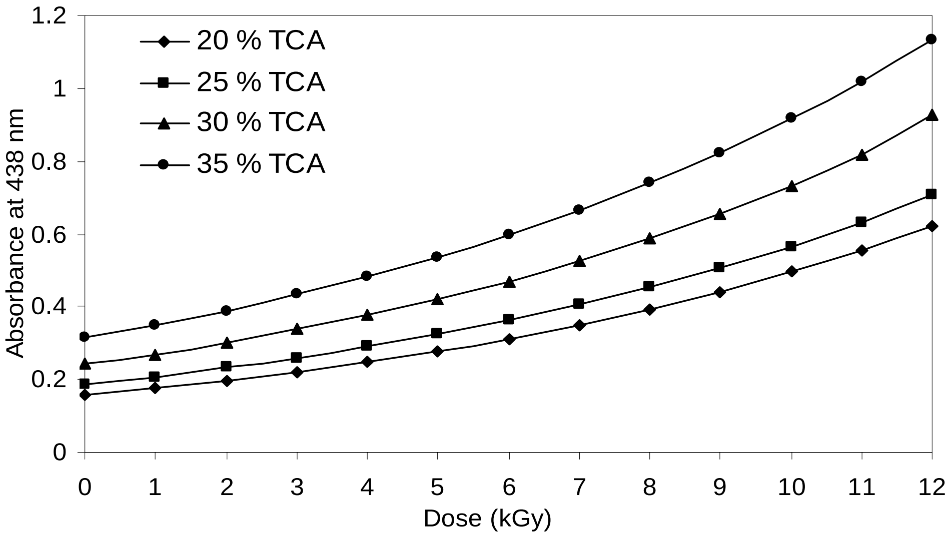


Fig. 5: Dose-response curves of PVA films for absorption band at 438 nm.

Fig. 6 and 7: The values of $D_0$ (kGy) of 575 nm and 438 nm absorption peaks for PVA film dosimeter at different TCA concentrations.

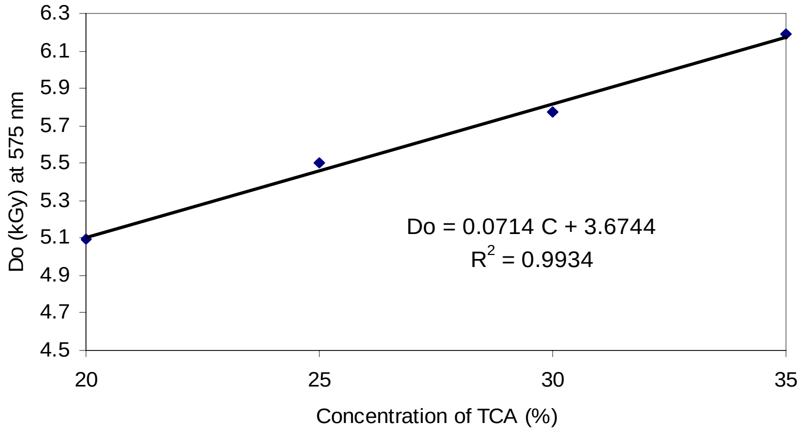


Fig. 6 The values of *D*o for absorbance at 575 nm.

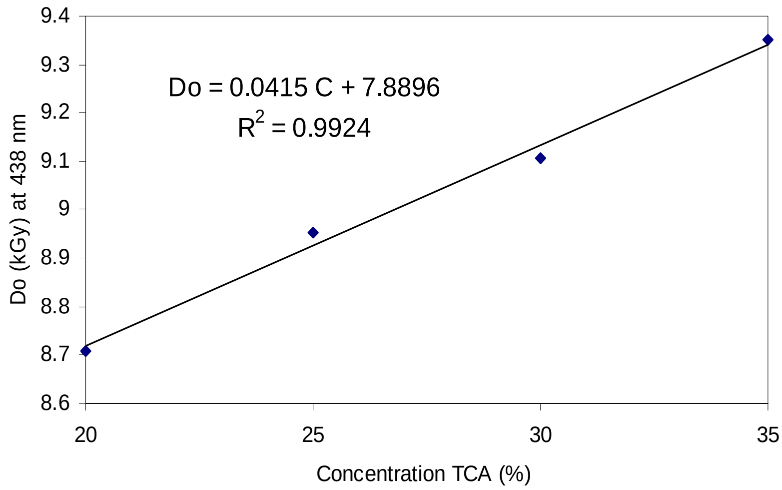


Fig.7 the values of *D*o for absorbance at 438 nm

## CONCLUSIONS

Radiation sensitive indicator based on cresol-red dyed PVA film dosimeters containing different concentrations of TCA have been developed and studied. The optical spectra produce two absorption bands peaking at 575 nm and 438 nm for low and high doses respectively. These polymer films undergo colour change from purple to yellow at dose depending on the concentrations of TCA. The dose-response curves show that for absorption bands at 575 nm and 438 nm the change in absorbance decreases and increases respectively with absorbed dose depending on TCA concentrations. The polymer films can be used as routine dosimeters in irradiation process for food preservation as their colour change from purple to yellow in the range from 5 kGy to 7.5 kGy. The spectrum analysis using Raman spectra suggests that the effect of radiation and the subsequent chemical reactions can be observed at the molecular level.

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