6 MV Photon Beam Induced Optical Properties of Dyed Polyvinyl Alcohol/Trichloroacetic Acid Blends

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Abstract: *The objective of the work is to study the effect of photon on the optical properties of dyed polyvinyl alcohol-trichloroacetic acid (PVA-TCA) blends prepared through solvent casting technique at radiotherapy dose. The films were cut into 2 × 2 cm^2 and kept away from direct sunlight at room temperature until irradiation process. The films were simultaneously irradiated with a 6 MV photon beam produced by linear accelerator Siemens MXE-2. The dose exposure given was set from 50 to 400 cGy. The optical properties were measured using the UV-visible spectrophotometer Shimadzu-1800, set at a wavelength range between 200 nm and 800 nm. The absorbance spectra were obtained with the existence of three absorbance band peaks at 273 nm, 444 nm and 582 nm. Initially, all absorbance increased with increasing dose applied. The results gained indicate that the optical energy band gap, E_g is equivalent to 5.20 eV while the absorption edge is 4.96 eV. These two parameters decreased with increasing dose. It is due to the increase of structural order between the conduction band and the valence band getting narrower. This also indicates that the film is undergoing a red shift. Hence, the value of Urbach energy, ΔE obtained is 0.089 eV, which increased with increasing dose since the lattice vibration depended on the applied dose. In conclusion, the PVA/TCA blends have a good optical characteristic in terms of dose response and optical transition.*

Keywords: Dyed polyvinyl alcohol-trichloroacetic acid, optical energy band gap, Urbach energy

1. INTRODUCTION

Solid polymer blends have been considerably studied in view of their wide potential application for novel systems and devices. With addition of dopant, blends or copolymers to the polymer matrix, the electrical, electrochemical and optical properties of the materials could be modified to achieve particular properties in various applications.[1] Furthermore, irradiation is known to cause

some induced lattice defects such as changing the colour centre in polymeric materials. The action of ionising radiation on polymers can result in cross-linking of the molecular chains, degradation of macromolecules and changes in the number and nature of the double bonds.[2] This entire process can occur either in one or all together, depending on the chemical nature of the polymer.

Polymeric films have been widely used in industry especially in the measurement of electron beam dosimetry.[3] Various studies have been done previously which had proven its effectiveness in detecting γ-rays, x-rays and electron beams with respect to industrial dose level. Since the polymeric film has been proven to be very successful in the industrial market, it is desirable to expose it to the medical market. Nevertheless, the doses used in the medical field are much lower compared to industrial. For that reason, referring to previous studies is not enough to assure the public about the reliability of the polymeric film as a dosimeter. Therefore, a research is needed in order to prove that the polymeric film will also perform well in the medical field which regularly uses energy. It is hoped that this study will be the starting point for an introduction of polymeric film to the medical practice such as radiotherapy.

The fundamental purpose of this project is to study the effect of photon on optical properties of dyed polyvinyl alcohol/trichloroacetic acid (PVA/TCA) blends prepared by solvent casting techniques at different doses.

2.   EXPERIMENTAL

PVA has been a polymer of choice for a long time in biotechnical and biomedical communities. It exhibits non-toxicity, noncarcinogenicity, and possess good biocompatibility and desirable physical properties such as elastic nature, high degree of swelling in aqueous solution and good film-forming properties. PVA is a biodegradable and biocompatible synthetic polymer with high water solubility and crosslink ability during hydrogel forming due to presence of hydroxyl groups in the polymer side chain.

2.1   Film Preparation

To prepare the stock solution, 0.08 g cresol red indicator was dissolved in 15 ml of 0.1 mol NaOH (M = 40.00 g mol^{-1}). To obtain a volume of 50 ml, ethanol was added to the solution. The mixed solutions were stirred at room temperature for 5 min to get a homogenous solution. For the main solution, 17.5 g PVA powder was dissolved in 350 ml distilled water. Next, the solution were stirred with the magnetic stirrer at around 75–90°C for 3 h.

After stirring, the solution was left to cool down to room temperature. 50 ml of PVA solution was added with 1 ml of stock solution and left overnight or with minimum of 12 h at room temperature. Before pouring the solution into a 15 cm × 15 cm glass plate, 1 ml of TCA was added to the mixture. The solutions were left to dry for around 6 days in room temperature and away from direct sunlight. The plastic film was peeled off from the glass plate and cut into 2 cm × 2 cm per piece, lastly being stored until irradiation. The average thickness of the film is 0.0197 mm. The initial colour of the film is yellow.

2.2   Film Irradiation

The films were exposed to photon beam produced by the linear accelerator machine. The irradiations were carried out at the radiotherapy department of Mount Miriam Cancer Hospital, Pulau Pinang, Malaysia. The energy level tested was 6 MV with a range of dose between 25 and 800 cGy. The arrangement of equipment is as shown in Figure 1. The source-to-surface distance (SSD) is set to 100 cm, with field size of 10×10 cm^2. The samples were placed simultaneously at the centre of the field size and irradiated simultaneously. Irradiation was carried out at room temperature.
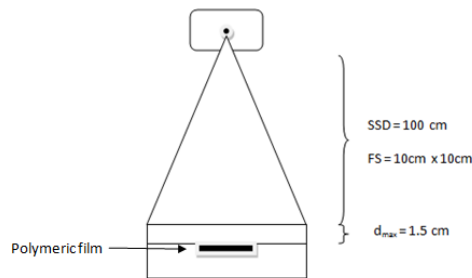

Figure 1:   The equipment arrangement during irradiation of sample where SSD is the source-to-surface distance, FS is the field size and d_{max} is distance at dose maxima.

2.3   Measurement

After irradiation, the films were measured by UV-visible Spectrophotometer-Shimadzu 1800 in the wavelength range of 200–800 nm using air as the reference in room temperature. Each sample was read three times with each reading set for 120 s.

3.   RESULTS AND DISCUSSION

Based on Figure 2, there are three peaks which are visible (273 nm, 444 nm and 582 nm). The maximum absorption in the spectrum was observed at 444 nm. Two of the peaks (444 nm and 582 nm) are within the visible range while the other peak (273 nm) is at the ultraviolet range. The absorption spectra transmitted two absorption bands in the visible region.[4]

These visible bands correspond to the excitation of outer electrons which provide information on the electronic transitions of the molecules in the samples. The absorbance of irradiated dosimeters decreases gradually with an increase of the absorbed dose.[5] The dominant absorbance band of UV region increases with dose. The absorption peaks at UV region were used to study the optical characteristics. The visible bands correspond to the excitation of outer electrons which provide information on the electronic transitions of the molecules in the blend samples. It relates to the excitation of the outer electrons, which can provide information on the electronic transitions between molecules in the blends samples.

According to Saion et al., these processes can be attributed to the π-π^{*} transitions from donor atoms (HOMO) to acceptor atoms (LUMO) because of the radiation-induced structural disorder in the polymer blends by the radiation scission of the blends and the presence of radiation-induced ions in the polymer.[7] Previously, Amrutha et al. and Zidan[12] studied the optical properties of pure PVA and and obtained a similar peak at 273 nm. They both agreed that the weak band is assigned to the carbonyl groups associated with ethylene unsaturation, which indicates the presence of conjugated double bonds of polyenes. Since the absorption does not occur at a long wavelength, a simple or unconjugated, chromophore indicated that this contains an O, N or S atom. In this study, it is referring to S atom from cresol red molecule.

The analysis of the optical absorption spectra can reveal the optical energy gap E_g between the CB and VB due to direct transition for both crystalline and amorphous materials. The absorption coefficient $\alpha(v)$ is a function of photon energy and obeys Mott and Davis's model:

$$\alpha(v)hv = B(hv - E_g)^{m} \qquad (1)$$

where B is a constant (also known as disorder parameter that depends on the transition probability and nearly independent of photon energy), E_g is the optical energy gap, hv is the energy of the incident photon while h is also known as plank constant and v is angular frequency of incident photon. Parameter m is the power coefficient with the value that is determined by the type of possible

electronic transitions during absorption processes. For instance, $m = \frac{1}{2}$, 3/2, 2 or $\frac{1}{3}$ for direct allowed, direct forbidden, indirect allowed and indirect forbidden respectively.
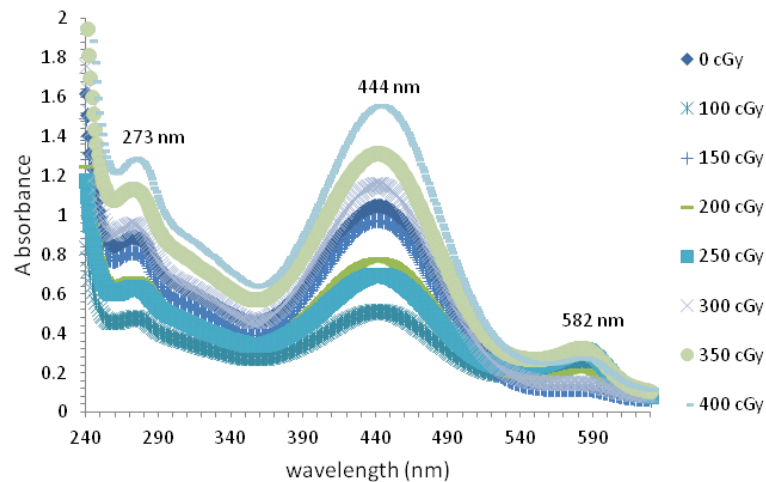

Figure 2: Absorption spectra of dyed PVA/TCA blends measured at wavelength range 240–630 nm for different doses.

Therefore, by using Equation 1, the direct optical band gap can be evaluated from the linear plots of $(\alpha h\nu)^2$ versus $h\nu$ graph. The extrapolation of the linear line part of $(\alpha h\nu)^2$ versus $h\nu$ graph for which $(\alpha h\nu)^2 = 0$ gives the direct optical band gap, which is the function of dose. The indirect optical band gap can be evaluated from the linear plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ graph at different doses. The extrapolation of the lines of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for which $(\alpha h\nu)^{1/2} = 0$ can give the indirect optical band gap as a function of dose. The indirect band gap graph is illustrated in Figure 3. The average energy band gap given from the extrapolation of the graph is 5.20 eV since the different in the band gap values range between 5.09 eV and 5.20 eV.

Figure 4 shows that the energy band gap decreases with increasing dose due to the increment degree of structural disorder. This is because the interaction of an electron with the polymer molecule will result in an excited state, followed by ionisation. Next, chlorine ions will form and react with the nearest H molecules and become HCl while double bonds (C=C) will be present in the polymer chain. This process will be continuous until chlorine is removed, as long as radiation is present. Hypothetically, from the density of state model, it is known that in amorphous case, when E_g decreases, the degree of disorder will increase. This concurs with the results from this study. Consequently, when the

dose increases, the spin density increases, hence more unpaired electron form in the unfilled band which result in the decreas of E_g values.
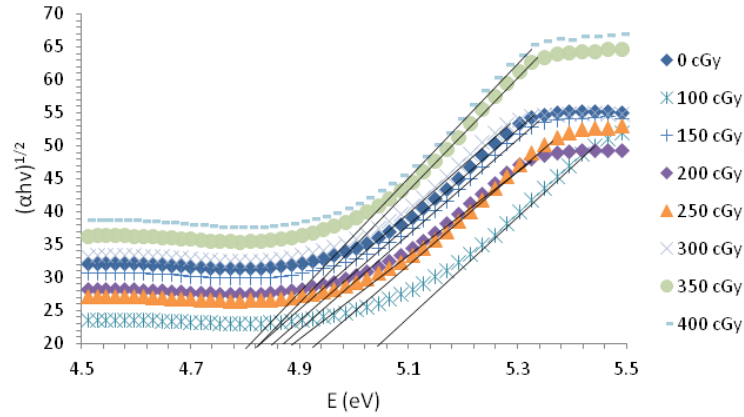

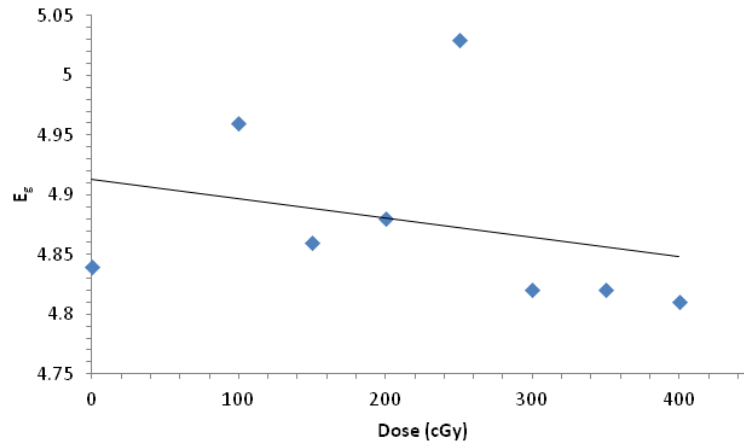Figure 3: The energy band gap, E_g of PVA/TCA blends at various doses.

Figure 4: The dependence of optical energy gap, E_g with different doses.

Susilawati and Doyan reported that both direct and indirect band gaps increase with TCA concentration and decrease with increasing dose.[9] However, the value of indirect band gap is greater than the direct band gap. According to Saion et al., the decrease in band gap energy with the increasing dose may be attributed to an increase in structural disorder of the irradiated polymer blends.[7]

The irradiation of polymer blends induces dehydroclorination, resulting in the loss of Cl and further cause ion detachment and creation of unsaturated group (–C=C–). These contribute to the structural defects, thus reducing the band gap as the dose increases. The decrease in E_g implies an increase in conductivity of

irradiated polymer blends. The optical energy band gaps (E_g) are dependent on dose and TCA concentration for both direct and indirect allowed transitions. The decrease in the energy band gaps (E_g) with increasing dose may be attributed to an increase in structural disorder of the polymer blends when the dose is increased. There is a shift of energy band gap (E_g) values towards lower energy with increasing dose that leads to a shift of optical activation energy (ΔE) value towards the lower/high energy with increasing dose.

Maged and Abdel Rehim found that the E_g values will decrease with increasing of γ-ray dose.[5] This is because γ-ray will increase the spin density and this results in more unpaired electrons in the unfilled bands following by the band tailing, which causes the decrease in forbidden energy gap. Hence, increasing the transition probabilities can be achieved by narrowing the optical energy band gap. Eventually, the Tauc model can be used as a standard model to determine the optical gap.[10] In this model, the disorder characteristic is assumed to relax the momentum conservation rule. Then, the square root distribution of conduction band and valence band were stated and also the momentum matrix element is assumed to be independent with hv.

Urbach Energy is a characteristic energy that determines how rapid the absorption coefficient decreases for below band gap energy. Urbach measured the absorption tail for different temperatures and showed that the Urbach Energy is approximately kT, the thermal energy.[11] The temperature dependence of the Urbach tail led to the conclusion that the below bandgap transitions are assisted transition. The Urbach tail can be caused by mechanisms other than phonon-assisted absorption. In other word, ΔE can be used to describe the "blurring" of the valence and conduction band. The equation used to determine ΔE describes the quasi-exponential slope of alpha around the band gap. The Urbach Energy, ΔE, is the energy width of the tail of localised states in the band gap was evaluated using the Urbach-edges method given by the formula:

$$\alpha(\omega) = \alpha_o e^{(hv/\Delta E)} \tag{2}$$

where α_o as a constant and hv is the minimum vertical energy difference between the valence and conduction bands. ΔE of irradiated samples were determined from the inverse slope from the straight lines of $ln\ \alpha$ versus photon energy hv.

From the measured sample prepared, by determining the inverse slope of the graph, the average value of ΔE obtained is 0.089 eV. Urbach Energy is usually interpreted as the width of the tail of localised states in the forbidden band gap.
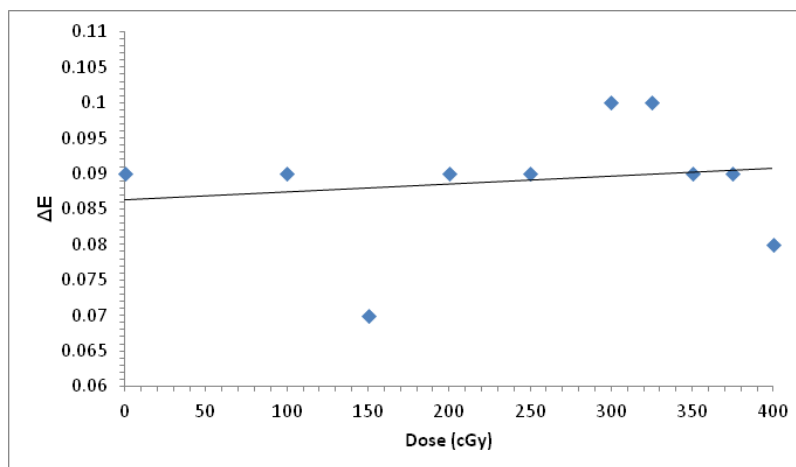
Figure 5:   The dependence of Urbach Energy, $\mathit{\Delta E}$ of the PVA/TCA blends at various doses.

As illustraated, Figure 5 displays the dependence of $\mathit{\Delta E}$ of the PVA/TCA blends at various doses. The addition of TCA to PVA enhances the electrical conduction of PVA host due to the ionic, electronic and impurity contributions arising from the TCA. The decrease and increase of $\mathit{\Delta E}$ in the sample can be understood by considering the mobility concept as proposed by Mott and Davis.[6] The fillers introduce additional defect states (e.g., colour centres) in the polymeric matrix. The density of localised states was proportional to the concentration of these defects and consequently to fillers.

4.   CONCLUSION

The effect of radiation optical properties of dyed PVA/TCA blends was developed and studied by using the UV-visible spectrophotometer. From the absorbance spectra obtained, there are three absorbance band peaks at 273 nm, 444 nm and 582 nm. These peaks correspond to the excitation of outer electrons and type of transition involved like $n \rightarrow \pi^*$ transition. The optical energy band gap, E_g obtained is 5.20 eV while the absorption edge is situated between 4.86 eV and 5.06 eV. These two parameters decrease with increasing dose. For optical energy band gap, E_g, the increase can be due to the increase of structural order, i.e., the structure was getting nearer between conduction band and valence band. Conversely, the value of Urbach Energy, $\mathit{\Delta E}$ obtained is 0.089 eV and increases with increasing dose. The dependence with dose since the lattice vibration depends on the provided dose. Basically, the PVA/TCA blends did have a good optical characteristic in terms of dose response and optical transition.

5.   ACKNOWLEDGEMENT

6.   REFERENCES

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