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Changes in the Optical Band Gap and Absorption Edge of Gamma-Irradiated Polymer Blends

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Abstract: The changes in the optical band gap and absorption edge of dyed poly(vinyl alcohol)-chloral hydrate (PVA-CH) polymer blends irradiated with gamma rays up to 12 k Gy have been investigated. The absorption spectra were measured in the wavelength range from 240 to 600 nm at room temperature. In the UV region, the absorption spectra increase with dose. The optical band gap (E_g) and the absorption edge decrease with increasing dose attributed to the structural disorder of the polymer blends due to dehydrochlorination of chloral hydrate with increasing dose. The energy width of the tail of localized states in the forbidden band gap was evaluated using the Urbach-edges method. It was found that the activation energy (ΔE) is less dependent on radiation dose but strongly dependent on concentration of the blend.

Key words: Gamma irradiation, polymer blends, absorption spectra, absorption edge, optical band gap, activation energy

INTRODUCTION

In recent years, studies on optical and electrical properties of polymer blend films have increased remarkably in view of their wide applications in radiation dosimetry and in optical and electronic devices[1]. The manufacturing of these materials can be tailored to have unique optical, electrical and electrochemical properties by irradiating with the electromagnetic radiation such as x- and γ-rays or the particulate radiation such as electron and ion beams in order to change their physicochemical properties through grafting and scission or dehydrochlorination[2-4]. Dosimetric characteristics of dyed Polyvinyl Butral (PVB)/chloral hydrate containing chlorine show change colour with increasing dose of γ-rays[2,5]. Detachment of C-Cl covalent bonds, results in the production of free radicals and ions. The subsequent chemical reactions lead to the formation of acids that allow the dye to change its structure and colour.

The increase of ionic species in polymer blends upon irradiation can be studied using absorption spectrometers, which provide details of the optical band gap energy and absorption edge and activation energy. The absorption spectra in UV region increase with increasing dose. In principle, photon with energy greater than the band gap energy will be absorbed. Electromagnetic wave packet interacts with electron in the Valence Band (VB), which is then raised across the band gap on the Conduction Band (CB) via two possible types of electronic transition, i.e. direct transition and indirect transition. In the direct transition the wave vector for the electron remains unchanged, while in the indirect transition the lattice vibration or phonons assist the transition so that the minimum of the CB lies in the different part of k-space from the maximum of the VB[3]. This study was concerned with the changes of optical band gap, absorption edge and activation energy with dose of dyed PVA-CH blend films irradiated with γ-rays.

MATERIALS AND METHODS

The film samples of the polymer blends were prepared using a solvent casting method. The PVA polymer powders (Mw = 70000, obtained from SIGMA, USA) were of research grade with the purity of 99%. The polymers were dissolved in double distilled water at 90°C and cooled at 30°C. Chloral hydrate [$CCl_3CH(OH)_2$, 2,2,2-trichloro-1,1-ethanediol] with the blending ratio of 23, 34, 45 and 57% (w/w) were added to the polymer solution. The blends were doped with cresol red dye to facilitate the radiation dosimetric study[6]. The polymer blends were

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solidified for about 72 h by solvent casting at room temperature. The average thickness of the films was found to be 70 μm.

The film irradiations were carried out in the [60]Co γ-rays chamber at the Malaysian Institute for Nuclear Technology Research Bangi, Malaysia. The absorbed dose rate was calibrated using Fricke dosimetry method to be 9.39 k Gy h[-1]. The samples were exposed at different doses up to 12 k Gy at room temperature.

The absorption spectra of the unirradiated and irradiated blend films were measured using a scanning double beam UV-visible spectrophotometer (Shimadzu, Model 1601) in the wavelength range 240-600 nm at room temperature. The absorbance A was calculated according to the Beer-Lambert Law equation $A = \log_{10} (I/I_0)$, where, I is the transmission intensity through the sample and I_0 is the intensity through the air gap as a reference. The absorption spectra are presented as the absorbance versus wave number.

RESULTS AND DISCUSSION

The absorption spectra show an increase and a decrease with increasing dose for blend concentration at 23% CH. Following irradiation the blend films undergo colour change from yellow at 438 nm peak to red at 529 nm peak, corresponding with the amount of acid formation (Fig. 1). These two peaks were used to determine dosimetric properties of the polymer blends, which have been discussed elsewhere[6]. The absorption peak at UV region, which increases with dose were used to study the
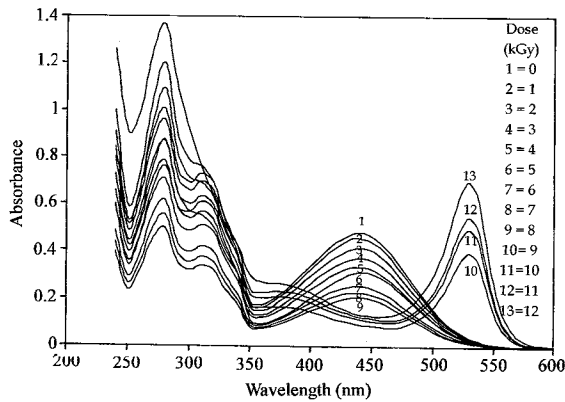

Fig. 1: Absorption spectra of dyed PVA-CH film at 23% blend concentration showing an increase in 529-nm absorption peak and a decrease in 438 nm peak with the increase of dose when it changes colour from yellow to red. However the absorption spectra at UV region always increase with increasing dose
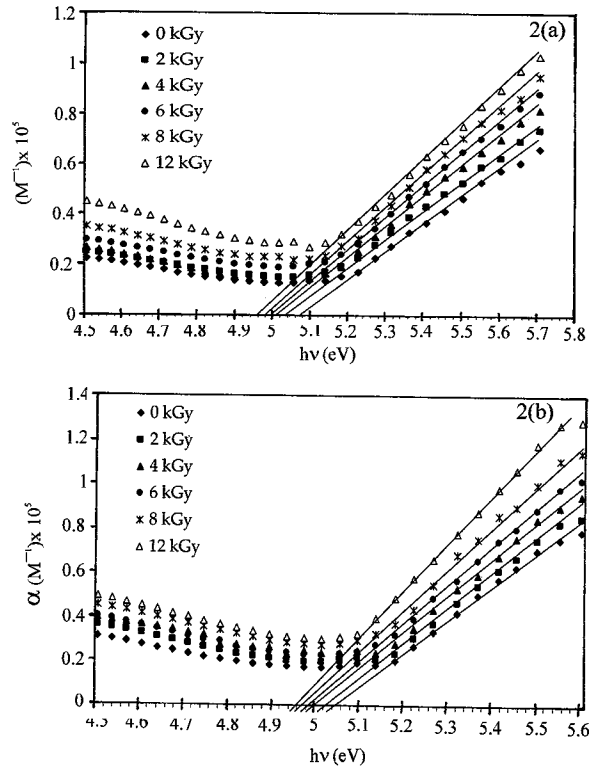

Fig. 2: Variation of α(v) vs. hv of the PVA-CH blends at various doses for (a) 23% and (b) 57% blend concentrations

optical characteristics. These bands relate to the excitation of outer electrons, which can provide information on the electronic transitions between molecules in the blend samples. They are 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[1] by the radiation scission of the blends and the presence of radiation-induced ions. The absorption coefficient α(v) of the PVA-CH polymer blends was taken from the optical absorption spectrum using relation:

$$\alpha(v) = 2.303 A/d \qquad (1)$$

where, d is the sample thickness in cm and A is the absorbance. The plots of α(v) vs. hv at different doses are shown in Fig. 2a and b for 23 and 57% CH concentration, respectively. The results show a continuous increase of α with increasing photon energy hv. Near the absorption edge, α increases more rapidly with hv. The absorption edge was determined by extrapolating the linear portion of α(v) vs. hv curve to zero absorption value[7]. The absorption edge decreases with increasing dose and
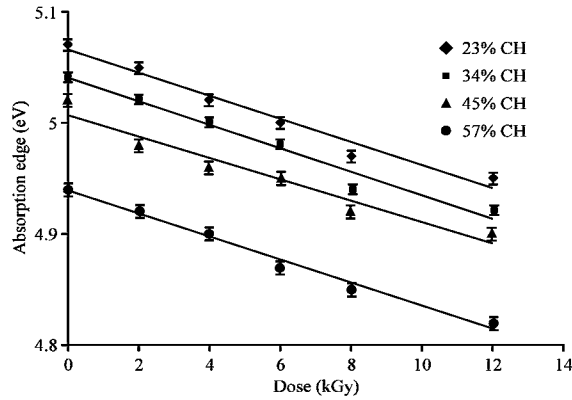
Fig. 3: Absorption edge position (eV) of the PVA-CH blends at various doses and blend concentrations

increases with CH composition. It was found that the absorption edge of 23% CH and 57% CH samples decrease from 5.08 to 4.96 eV and 4.85 to 4.62 eV, respectively, when the dose increases from 0 to 12 k Gy (Fig. 3). Abdel Fatah *et al.*[8] have measured the absorption edge of unplasticized poly(vinyl chloride) (UPVC) and they found that the value decreases from 4.35 to 2.04 eV when the fluence of 25 MeV proton beam increases from 10^{+13} to 10^{+15} ions cm^{-2}.

Analysis of the optical absorption spectra can reveal the optical energy gap E_g between the CB and the VB due to direct and indirect transitions for both crystalline and amorphous materials. The absorption coefficient $\alpha(v)$ is a function of photon energy and obeys Mott and Davis[9] model.

$$\alpha(v)hv = B(hv-E_g)^m \qquad (2)$$

where, h is the energy of the incidence photon, h is the Planck constant, E_g is the optical energy band gap, B is a constant known as the disorder parameter which is nearly independent of photon energy. Parameter m is the power coefficient with the value that is determined by the type of possible electronic transitions, i.e. m = ½, 3/2, 2 or 1/3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden, respectively[10].

The direct optical band gap can be evaluated from the linear plots of $(\alpha hv)^2$ versus hv at different doses as shown in Fig. 4a and b for 23 and 57% CH composition, respectively. The extrapolations of the lines of $(\alpha hv)^2$ versus hv for which $(\alpha hv)^2 = 0$, give the direct optical band gap, which is a function of dose as shown in Fig. 5. The optical band gap increases with increasing dose and CH concentration. The results show E_g decreases with increase of both the dose and the CH composition. It was found that E_g at 0 Gy reduces from 2.50 eV for 23%
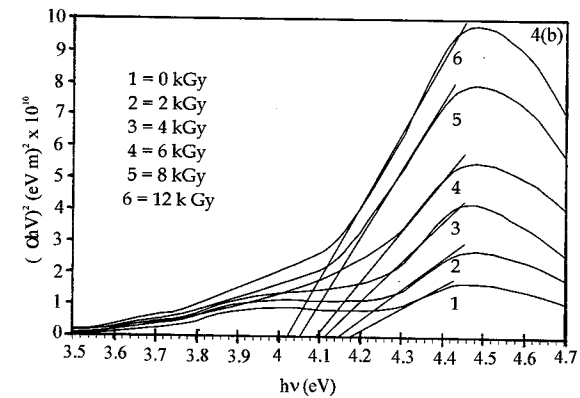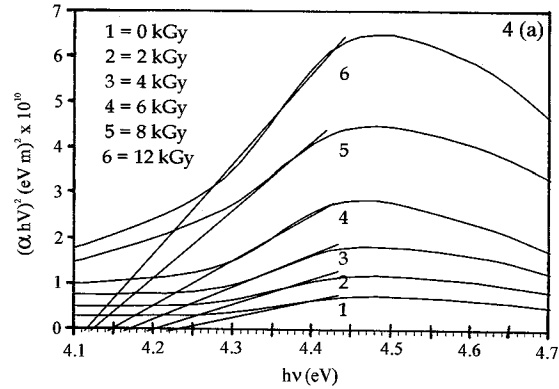

Fig. 4: Variation of direct allowed transition $(\alpha\ hv)^2$ vs. hv of the PVA-CH blends at various doses for (a) 23% and (b) 57% blend concentrations
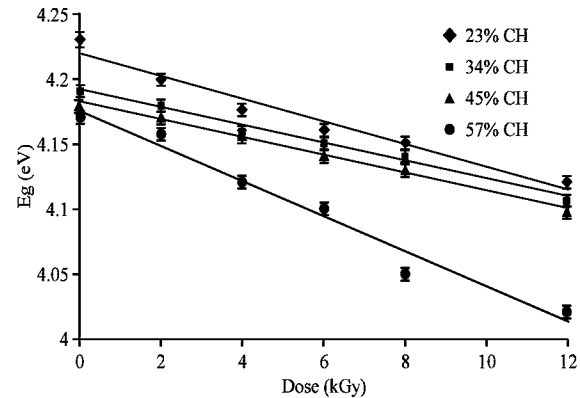

Fig. 5: Variation of the optical band gaps with increasing dose of the PVA-CH blends at 57% blend concentrations

to 2.25 eV for 34% CH composition. At 12 k Gy the value reduces further from 2.38 eV for 23% to 2.22 eV for 34% CH composition (Fig. 5). A decrease in the band gap energy with increasing dose may be attributed to an increase in structural disorder of the irradiated polymer blends. Irradiation the polymer blends induces dehydrochlorination of chloral hydrate, resulting of loss
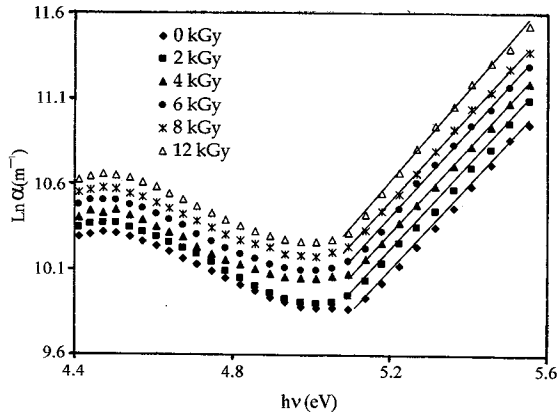
Fig. 6: The optical activation energy ΔE of the PVA-CH blends at various doses and blend concentrations
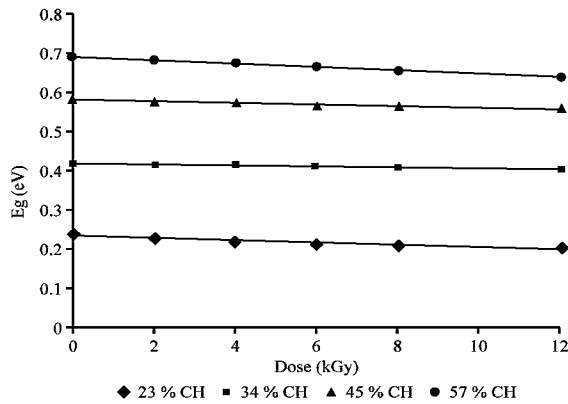

Fig. 7: The optical activation energy ΔE of PVA-CH blends at various doses and blend concentrations

of Cl and induce ion detachments and unsaturated group (-C=C-). These contributed to the structural defects, which reduce the band gap with increasing dose[1,8]. The decrease in E_g implies an increase in the conductivity of irradiated polymer blends. Some researchers have reported the change in band gap energy of some materials irradiated with γ-rays and protons. The value of E_g varied from 2.59 to 2.49 eV for manganese Phthalocyanine (MnPc) irradiated with γ-rays up to 25 k Gy[1], from 3.75 to 3.45 eV for tellurium dioxide (TeO$_2$) irradiated with low doses γ-radiation up to 40 Gy[1]. It varied from 4.35 to 2.04 eV for UPVC films irradiated with proton beam of increasing fluence from 10^{+13} to 10^{+15} ions cm^{-2}[8].

The optical activation energy, ΔE, is the energy width of the tail of localized states in the band gap was evaluated using the Urbach-edges method given by the formula:

$$\alpha(\omega) = \alpha_0 \exp(\hbar\omega/\Delta E) \qquad (3)$$

where, α_0 is a constant and $\omega = 2\pi v$. The activation energy ΔE of irradiated samples were determined from the slope of the straight lines of $\ln(\alpha)$ versus photon energy hv of Fig. 6 for 57% CH composition. The results of ΔE values at different doses are shown in Fig. 7. It can be seen that ΔE is strongly dependent on CH composition but is less dependent on dose. It was found that ΔE at 0 Gy increases from 0.24 eV for 23% CH to 0.42 eV for 34% CH composition and then to 0.69 eV for 57% CH composition. At 12 k Gy the value increases from 0.20 eV for 23% CH to 0.40 eV for 34% CH and then to 0.64 eV for 57% CH. It has been reported that ΔE value increased from 0.5 to 0.98 eV for manganese Phthalocyanine (MnPc) irradiated with γ-rays up to 25 k Gy[1] and for UPVC films irradiated with proton beam of increasing fluence from 10^{+13} to 10^{+15} ions cm^{-2} the value increased from 1.18 to 1.93 eV[8].

CONCLUSIONS

The absorption spectra of irradiated PVA-CH polymer blends in UV region increase with the increase of dose. The interaction of gamma radiation with the polymer blends induces dehydrochlorination of chloral hydrate, resulting ion detachments and formation of unsaturated group, which contribute to the structural defects in the polymer blends. The absorption edge and the optical band gap energy (E_g) decrease with increasing dose. However, the activation energy (ΔE), the energy width of the tail of localized states in the band gap, is less influence by the radiation action.

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