Radiochemical Properties of Irradiated PVA\AgNO$_3$ Film by Electron Beam

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Abstract: ***The PVA bulk solution was first prepared by dissolving PVA powder (5 wt %) in distilled water under controlling water bath temperature at 60-70 0C and continuous stirring for 3 hours, After the solution cooled down to ambient temperature, a concentration of (0.01and 0.03 wt%) of AgNO3 were added to solution in a darkroom and stirred for 2 hours, then the blend solution is poured into Petri dishes and allowed to dry to form films by casting under ambient temperature for 3 days in a darkroom, after draying the films were cut to 2cmx2cm and kept in black pags. The films were exposed to different doses (2, 4, 6, 8, 10 Gy) from a linear accelerator by constant energy 6 MeV with applicator cone and SSD (applicator surface distance) 50 cm, field size 10cmx10 cm. The characterization by by UV-visible spectroscopy showed that the pure PVA has an absorption peak in the range of ultraviolet at 275 nm and the absorption peak increases with radiation dose increment from 0 to 10 Gy and the composites films (PVA\AgNO3) showed an absorption peak coefficient at 420 nm (visible light) which is also increases as the radiation dose increases. Also the energy band gap of the composites irradiated films appeared to be decreases from 4.0E-19 down to 3.5E-19 eV. Moreover the optical density of the irradiated films showed significant correlation (R2 = 0.99) with the applied dose. While the tensile strength (TS) of the irradiated PVA film has been increases following the increment of radiation dose and peaking at 30 MPa at 6 Gy, then decreases as the dose increase. The study also revealed that there is a significant (R2 =96) linear proportional relationship between the absorption coefficient and the applied dose on the PVA film.***

Keywords: Polymer, films, Radiation, Processing**.**

1. Introduction

In the realm of radiation detection, any materials possess properties of response to radiation could be used as a radiation detector and the variation between materials and their worth consideration as detector is ascribed to their sensitivity to detect low level of radiation and the fast response.

One of interesting materials related to such field is the polymer hybridized with metal nano particles, in particular silver nano particles which exhibit unique optical, electronic, and electrochemical properties that answer many potential applications in optical waveguides, optical switches, molecular identification, oxidative catalysis, antimicrobial effects, etc. [1]. These interesting properties are strongly dependent on the particle sizes and shapes and therefore methods of synthesizing silver nano particles should be able to control these parameters.

Silver nano particles embedded in polymer matrix such as poly (vinyl alcohol) (PVA), poly-methyl-methacrylate (PMMA), and polystyrene have been reported by some authors [2]-[3]. Also in this realm Ali et al, [4] studied the effect of electron beam irradiation on the structural properties of Poly (Vinyl Alcohol) formulations with Triphenyl Tetrazolium Chloride Dye (TTC) under various radiation doses. The results showed that at a dose of 50 kGy, the color difference (ΔE) of PVA/TTC films was increased by -10 times of the initial value. As well the presence of the TTC dye caused a depression in the melting point (Tm), heat of fusion (ΔHf) of the PVA bulk polymer, improved the thermal stability of PVA and also the tensile strength at break of PVA/TTC composites was improved after electron beam irradiation. Electron beam irradiation of polymer materials is a controlled technique that mainly induces various effects in view of chemical modification such as displacing atoms, carbonization, production of free radicals, cross-linking and chain scission that gradually and continuously modify or degrade the structural, morphological, optical and mechanical properties of polymer electrolytes and composition [5]-[6]. The induced chemical and optical properties in polymer-metal composites rendering the composites as conductive or semi-conductive materials hence it gives the opportunities for the use of these materials in potential applications, such as fabrication of integrated circuits, optoelectronic devices, sensors, ion detecting devices, solid-state batteries and other technological applications [7]. The view of this study is to reveal the effect of electron beam irradiation on polyvinyl alcohol hybridized with silver metal which is seemed to be differing from the technical preparation of same materials by gamma irradiation, as the last technique needs buildup materials to induce the specific effect.

2. Methodology

The PVA bulk solution was first prepared by dissolving PVA powder (5 wt %) in distilled water under controlling water bath temperature at 60-70 C and continuous stirring for 3 h. the solution cooling down to ambient temperature, concentration (0.01, 0.02 and 0.03 wt%) of $AgNO_3$ is adding to solution in a darkroom and stirred for 2 hours, then the blend solution is poured into Petri dishes and allowing to dry to form films by casting under ambient temperature for 3 days in a darkroom after dray cutting the film to 2cmx2cm and butting in the pocket films. After prepare the films, we take the film and exposure to different doses (2, 4, and 6 Gy) from a linear accelerator by constant energy 6Mev with applicator cone and SSD (applicator surface distance) 50 cm, field size 10cmx10 cm and use UV- spectrophotometer to measure the intensity of electron beam passing through and compares it to the intensity of electron beam before it passes through the film. Tensile strength (TS) of the PVA film has been carried out using Universal Testing Machine (INSTRON, model 1011, UK). The load range was 500 Newton (10 mm/min crosshead speed and 30 mm gauge length). The dimensions of the test specimen were 10cm × 5 cm × 0.2 mm.

3. Results and Discussion

Figure 1 shows the UV-visible spectrum for pure PVA irradiated with 0 – 10 Gy. It shows that the pure PVA has an absorption peak in the range of ultraviolet at 275 nm. And such absorption peak increases with radiation dose increment from 0 to 10 Gy. The increment of absorption by pure irradiated PVA ascribed to high density and toughness of the film formed by irradiation such as cross linking and grafting [8]. Also the tensile strength of the PVA/Ag composite Figure (2) has been increases following the increment of irradiation and peaking at 6 Gy then decreases as the dose increase, such phenomena could be ascribed to cross linking and bond session respectively [9]. The cross linking would lead to an increment of absorption coefficient [4].

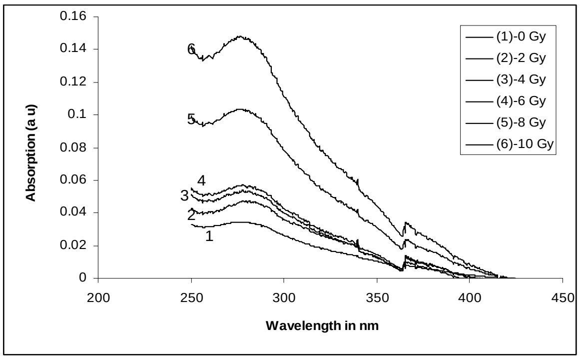

Figure 1: Shows the UV-visible spectrum for pure PVA irradiated with gamma radiation doses of 0 – 10 Gy

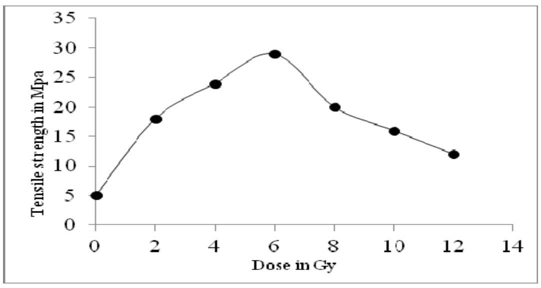

Figure 2: Shows the PVA tensile strength in MPa versus different radiation dose in Gy

Figure 3 shows the correlation between the dose and the absorption coefficient for the irradiated pure PVA. It shows that there is a linear proportional relationship between the absorption coefficient and the applied dose on the PVA film of the form: $y = 0.01x$, where *y* refers to absorption in (a u) and x refers to dose in Gy. Such significant relation (R^2 = 0.96) indicates the obvious effect of radiation on the PVA. Same result has been mentioned by [10] Mohammed et al, (2011).

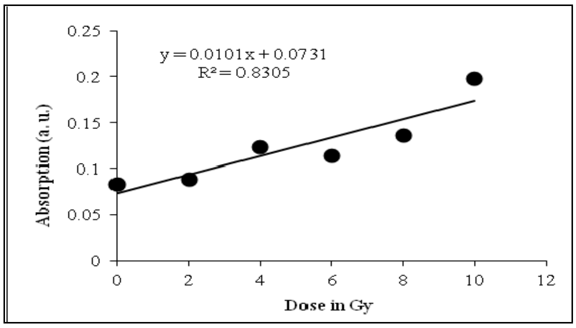

Figure 3: Shows the correlation between the dose and the absorption coefficient for the irradiated pure PVA.

Figure 4 shows the UV-visible spectrum for PVA/Ag film irradiated with electron beam receiving radiation doses of 0 – 10 Gy. It shows that there are two prominent peaks at the wavelengths (λ) 275 and 420 nm which are related to criteria of the pure PVA and PVA/Ag after irradiation respectively. The absorption band peaking at 420 nm occurs in the visible light band and such peak increases as the radiation dose increases from 0 up to 10 Gy. The corresponding visual color for the peaks at 420 nm was light yellow turned to golden and light brown after irradiation as shown in Figure (5)

The UV–Vis absorption spectra further indicates the formation of Ag nano particles due to electron irradiation. The characteristic peak of the Ag nano particles appears in the range of 400 to around 440 nm, depending on the value of electron doses which is caused by surface plasmon resonance [11]. The surface plasmon phenomenon, i.e., cloud electromagnetic waves coupled with the conduction band (CB) electrons, shows the peak at 420 nm shifting to lower wavelength and indicating a decrease of grain sizes of Ag nano particles within the PVP solution following the reduction at higher doses (π*¬π transition) [12].

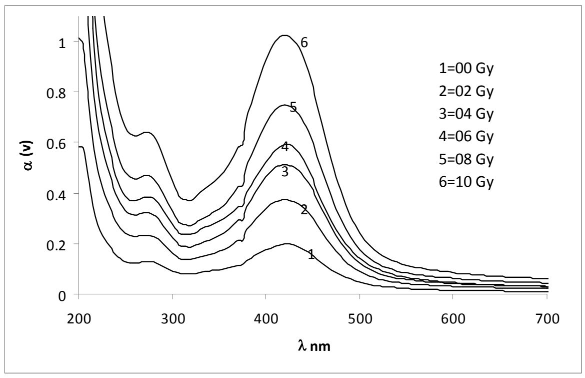

Figure 4: Shows the UV-visible spectrum for PVA/Ag film (Ag= 0.01g) irradiated with electron beam doses of 0 – 10 Gy.

Figure 5 shows the prepared composites film of PVA/Ag^+ at different electron radiation doses, in which the white color of the film has been changed to yellow, golden and dark green following the radiation steps up to 10 Gy such color change has been reported by Vladimir et al, [13]. The color change of the film reveals different reduction stages of silver ions by irradiation [14]-[15]. The absorbed radiation energy in the media resulted in the formation of reactive species such as hydrated electron (e^-_{aq}), hydrogen atom radical (H^o) and hydroxyl radical (OH^o). Among these species, (e^-_{aq}) and (H^o) are very powerful reducing agents, hence both of them reduce Ag^+ ions within the PVA binder into metallic silver according to the reactions (1 and 2) as stated by Ramnani et al, [16].

$Ag^+ + e_{aq} = Ag$ (1)
$Ag^+ + H^o = Ag + H^+$ (2)

Figure 5: Shows the PVA/Ag film (first raw was 0.03 Ag gram and second raw was 0.01 gram) irradiated with electron beam and receiving doses of 0 – 10 Gy.

Figure 6 shows the correlation between the absorption coefficient at λ= 275 and λ=420 nm and the applied radiation dose. It shows that the absorption coefficient at 420 nm (visible light) and 275 nm (ultraviolet light) increase linearly with increment of applied radiation dose based in equations: $y = 0.08x + 0.2$ and $y = 0.05x + 0.1$ respectively, where y refers to absorption in (a u) and x refers to dose in Gy. The prominent peaks at 420 and 275 nm indicate the sensitivity of the PVA/Ag composite to radiation. The strong relationship between the applied dose and the absorption (R^2 = 0.97) could deduced the possibility of utilizing the composite film as radiation detector and monitoring as has been proposed by Mohammed et al, [10].

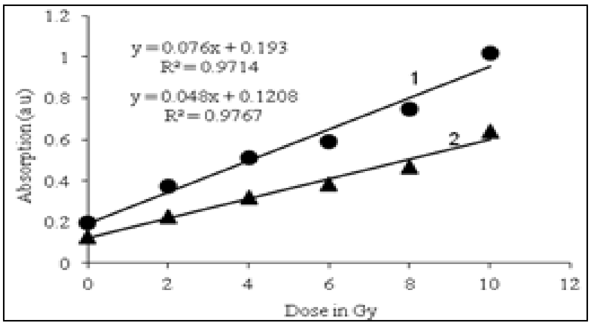

Figure 6 shows the correlation between the absorption coefficient at λ= 275 and 420 nm and the applied radiation dose.

The relation between the optical absorption coefficient (*α*) for a direct transition and the photon energy (*hv*) was given by Fahrenbruch and Bude, [17]; Mott and Davis, [18] as shown in equation (3).

$\alpha hv = A(hv - Eg)^{1/2}$, (3)

Where *A* is a constant, *h* is Planck's constant; *v* is the frequency of the radiation and E_g is the optical energy gap. For the determination of the direct optical band gap, $(\alpha hv)^2$ was plotted as a function of photon energy (*hv*) and the curves have been extrapolated to intersect at α = 0 as shown in Figure (7), hence the E_g has been determined and observed to be reduce following the radiation dose increment from 4.0E-19 down to 3.5E-19 eV. Such reduction in the band gap has been shown by Subramanya et al, [19].

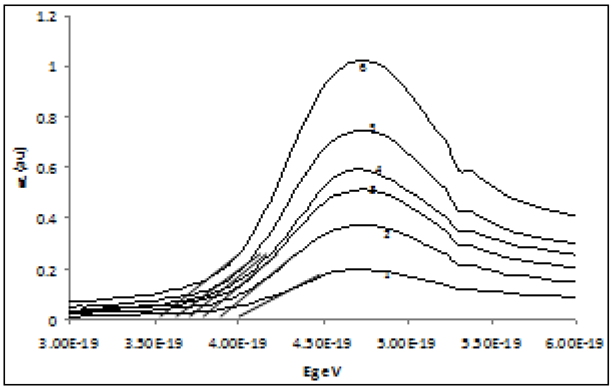

Figure 7: Shows the extrapolation of α (*v*) versus E_g (eV) to deduce the energy band gap.

Figure 8 shows the correlation between the optical density and the applied dose in the range of 0-10 Gy at peaks of wavelengths 275 and 420 nm. It shows that there is linear proportional correlation between the two parameters in the absorption band of 275 and 420 nm, however the relation of absorption in the range of 420 nm is strong as R^2 = 0.99, which ascribed to the sensitivity of the silver to radiation and further more encouraging the application of PVA/Ag film as a detector or monitoring based on the optical density change. And the correlation could be fitted to the equation of the following form: $y = 0.01x + 0.07$, where *y* refers to OD and *x* refers to the applied dose in Gy.

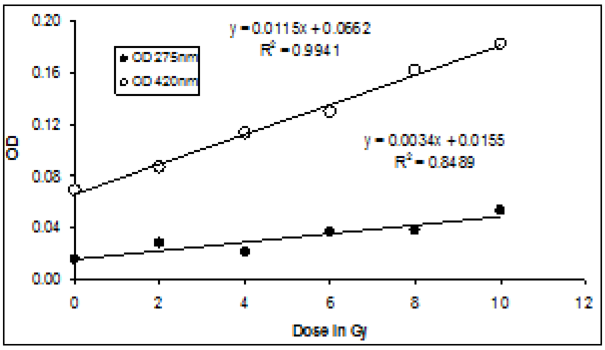

Figure 8: Shows the correlation between the optical density and the applied dose in the range of 0-10 Gy at peaks of wavelengths 275 and 420 nm.

4. Conclusion

The irradiated PVA\AgNO$_3$ composites in a form of films could be utilized successfully as radiation detector based on the excellent optical properties i.e. absorption coefficient in which the relation follows the equations of the form $y = 0.08x + 0.2$ at λ = 420 nm and $y = 0.05x + 0.1$ at λ = 275 nm ('x' *refers to radiation dose in Gy and 'y' refers to absorption coefficient*)., and the optical density in which the relation follows the equation of the form $y = 0.01x + 0.02$ at λ = 420 nm ('x' *refers to radiation dose in Gy and 'y' refers to optical density*). Also the application of irradiation could rendering the insulator composites to semiconductor or conductor by reducing the energy band gap as well could induce stiffness or rigidity in the composite film of PVA\$AgNO_3$.

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