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Preparation and Characterization of Polyvinyl Alcohol /Thymol Blue/Cuprous Oxide Films Proposed for Diagnostic Radiation Detection

Maged S. Al-Fakeh,[a*,d] Mohammed Ahmed Ali Omer,[b*,e] AbuzarAlbadri,[a] Abdulrahman A. S. Alsayyari, [b] and Ahmed F. Elhag[c]

[a] *Department of Chemistry, College of Science, Qassim University, Buraidah 51452, Saudi Arabia*
[b] *Department of Radiologic Technology, College of Applied Medical Sciences, Qassim University, Buraidah, 51452, Saudi Arabia*
[c] *Department of Physics, College of Sciences, Qassim University, Buraidah, 51452, Saudi Arabia*
[d] *Taiz University, Taiz 3086, Republic of Yemen*
[e] *College of Medical Radiological Sciences, Sudan University of Science & Technology, Khartoum-Sudan*

Abstract

Background: Usage of low radiation is indispensable, hence accurate measurement became inevitable for radiation practitioners and patients. The current study presents the synthesis and characterization of polyvinyl alcohol doped with Thymol Blue and Cuprous Oxide (PVA/TB/Cu_2O) as nanocomposite films for low radiation dosimetry.
Method: films prepared under controlled parameters (PVA 5%, temperature 80 ºC, 0.01 g of TB and 0.2 g of Cu_2O). The films were irradiated with X-ray (0, 2, 4, 6, 8, 10 mGy) and evaluated using UV-spectroscope, XRD, and FTIR.
Results: UV- spectroscope for (PVA/TB) films showed absorbance peaks at l = 435, 326 and 279 nm, which de-creased as the radiation dose increased. (PVA/TB/Cu_2O) films showed absorbance bands at l = 265 & 370 nm, which increased as the radiation dose increased. XRD for (PVA/TB) reveals the crystallinity of PVA at 2 thetas = 200 which increased by 55% at 10 mGy. The PVA/TB/Cu2O composite films present a prominent peak at 2 Thetas = 350, which increases following the radiation doses. The FTIR spectroscope showed chemical bonds (CH, C-O, C-O-C, CH2, C-OH, C=O, C≡N, and OH) intensities that degraded as the radiation dose increased.
Conclusion: the composite of PVA/TB ± Cu_2O is utilizable for radiometer based on optical and chemical changes.

Keywords: Radiation, Measurement, Diagnostic, Polymer, Films.

1. Introduction

Radiation dosimetry has been one of the most important tasks for the radiation practitioner in charge; as it deals with controlling exposure dose for diagnostic purposes as well as for radiotherapy applications. The radiation dosimetry for the low radiation levels such as the diagnostic range still faces great challenges in view of optimization and assessment of exposure dose consequences (radiation sickening). Therefore, the research and attempt for dosimetric foundation and means of radiation measurement are still in need and have to persist. Relative to the necessity for radiation measurement and dosimetry, there have been many attempts of scholars, whom their endeavors serve the field in different aspects. One of the promising materials that can be used for radiation dosimetry, measurement, and many other medical applications is the polymer and polymer composites [1]. The possibility of using this material for radiation dosimetry is recon on the possible induction of physio-chemical changes and the sensitivity of the material to radiation; in addition to accuracy, reproducibility, tissue equivalency, absolute dose reading, specificity, and linear response …etc. [2].

The radiation dosimetry of polymers basically depends on the induced chemical changes (bond session, polymerization, grafting, crosslinking), while the physical changes depend on the change of optical properties which further could depend on the doping materials such as (silver nitrate, cuprous oxide, ferrous oxide, organic dye … etc).

*Corresponding author e-mail: Email: m.alfakeh@qu.edu.sa; ma.omer@qu.edu.sa ;(Maged S. Al-Fakeh).
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With reference to previous studies in this field, there were tremendous works, some have been factually applied and some with potential feasibility, and others still remain as hypotheses. Regarding the applied ones in the range of high doses, Khalid et al, [3] prepared radio-chromic polyvinyl alcohol (PVA) gel doped with different concentrations of methyl thymol blue (MTB) and rendered as films that responded to gamma irradiation in the form of quenching or bleaching of the solution color by increasing the radiation dose. In the same realm, Doyan et al [4] prepared a polyvinyl alcohol (PVA) gel doped with trichloroethylene, and cresol red dye which was further assembled as the film for gamma radiation dosimeter. Their prepared films respond to gamma-ray exposure (0, 2, 4, 6, and 12 kGy) as (industrial applications) from the Cobalt-60 isotope and are rendered to yellow color. Also, Ibrahim et al [5] prepared polyvinyl alcohol (PVA) gel doped with silver nitrate (AgNO3) and fabricated as the film for therapeutic radiation detection and applications. The films were irradiated with gamma rays in the dose range 0-10 Gy (therapeutic range) to induce applicable industrial applications. They proved their product after Thermo-gravimeter analysis and scanning calorimetric. They end up that the addition of $AgNO_3$ led to a more compact structured film compared to the pure PVA with improved thermal stability up to 358.9 C^o and increased isotropic character of the polymer samples. And accordingly, those researchers recommend that: this product could have foreseen applications in different electronic and semiconductors applications. A further study was carried out by Mohammed & Emad, [6] to prepare a polyvinyl alcohol (PVA) gel doped with cuprous oxide (PVA/Cu2O) which was furtherly formulated as the film for the measurement of radiation based on the changes of optical properties. The films were irradiated using a gamma radiation source of (1, 2, 4, 6 … 12) Gy (Therapeutic dose). The films were investigated using an ultraviolet-visible spectrophotometer, which revealed a differential alteration in the hue of color in exposed films from pinky to dark brownish. Also, the prominent peaks at 215 and 415 nm (absorption), and the optical density of films increase as the dose increased. As recent study; Alashrah et al, [7], have prepared a radiation detection film derived from PVA gel doped with Nitro Bule Tetrazolium that depends on Opto-chemical and morphologic changes.

For the importance of estimating the tissue response to radiation therapy and radiation protection, several measuring systems have been pioneered, which include Ionization chambers, Thermoluminescence dosimeters, Silicon diodes, Radiographic film, and polymer detectors (Dosimeters) [8-11].

The current trend of this study, aimed and focused on the fabrication of polymer as PVA impregnated with Thymol Blue (TB) dye and Cuprous Oxide solution which was later formulated as the film to be utilized as low radiation detection and measurement i.e. in diagnostic range dosimeter. This method adapted from the effect of radiation in the dry state of the polymer composites, such as induced physical and chemical changes. These induced effects can be visualized, measured, and quantified with the usage of various systems such as; UV-visible spectroscope, XRD, IR spectroscope, optical densitometer … etc. The induced quantified effects due to radiation exposure furtherly could be correlated with indexed values of exposure doses. Such correlation could be utilized as a reference meter for many systems and personnel doses. In addition to other applications such as a shield or anti-ultra violet radiation barrier or controlling the level of ultraviolet radiation, in addition to the utilization of wavelength subtraction technique or dopant mixture.

2. Experimental

2.1. Materials and Methods:

2.1.1. Materials

- Compounds of Polyvinyl alcohol (PVA) $[CH_2CH(OH)]n$ with (MW 85,000 to 124,000), Cuprous Oxide (Cu_2O) with a MW of 143.09 g/mol, Thymol Blue (TB) ($C_{27}H_{30}O_5S$) with a MW 466.59 g/mol, have been dispensed from the company of Abdullatif H. Abujadayel& Sons – KSA.

2.1.2. Equipment

- X-ray machine model (GE, healthcare, model Al01C II, July/2011- S. N: 3758, German)
- Ultraviolet spectroscope model UV-2600, with a scanning range of 200 to 1100 nm.
- XRD diffractometer, model (Rigaku XRD, Ultima IV, USA): having the following exposure factors: 40 kVp, 30 mA, anode material was Cu Ka (λ =1.54180 Å).
- IR - spectroscope: model Agilent tech with Gladi-ATR, USA), 200 to 4000 cm^{-1} with 20 scans and a resolution of 4 cm^{-1}.

2.1.3. Technique

2.1.3.1. Doping of polymer composite

The compound of PVA solution was prepared as 5% of a PVA in distilled water and stirred in hot water at 70 ^oC for 3 hours in a beaker then left to cool in ambient temperature. And some weights of 0.01 grams of TB were added in different that contained 100 ml of PVA and stirred for 4 hours in a dark room. Then an amount of 0.2 g of Cu_2O was added to the solution mixture and stirred for 7 hours in a dark room. Then some volumes of 10 ml from each

mixture of (PVA/TB 0.01 gram) and (PVA/TB/Cu_2O 0.2 grams) were sucked and poured into some Petri dishes and kept on a true flat surface (adjusted by a level of water meter). The samples were left for 3 days to dry a darkroom. Then the films were peeled off from Petri dishes, formulated into pieces (1.0 × 1.0 cm), loaded in envelopes, and transferred to the stage of irradiation.

2.1.3.2. Irradiation & Technique

The irradiation was done by x-ray from the selected x-ray machine, all the enveloped films re-ceived exposure doses as 0, 2, 4, 6, 8, and 10 mGy. Based on the exposure factors (KV 67, mAs 2.5, filter Cu: 0.1 mm, distance 100 cm, field size 8 × 8 cm) that resulted in a dose of 1.0 mGy. Such ex-posure has been repeated to attain the specific doses (0, 2, 4, 6, 8 and 10 mGy). The films were load-ed between buildup of tissue equivalent material with 0.4 cm thick.

3. Results and discussion

The UV-visible spectrum for the films consisting of PVA 5%/0.01 gram of Thymol blue composite showed three preeminent peaks of absorption coefficient (α) at λ = 435, 330 and 280 nm. However, these peaks decreased following the increment of radiation doses from 2 – 10 mGy (Fig. 1). These relative reductions in the absorption coefficient of the polymer composite films at λ = 435, 330 and 280 nm have significant (R^2 = 0.96) linear relationship with the amount of the applied radiation dose (Fig. 2) which is considered as one of the important properties of the dosimeter as well as a tissue equivalent and shaping [12]. The decreasing absorption could be ascribed to the induced bone session by irradiation [13]. However, such a fact could stimulate and encourage the applications of TB as a potential promising media for radiation detectors.

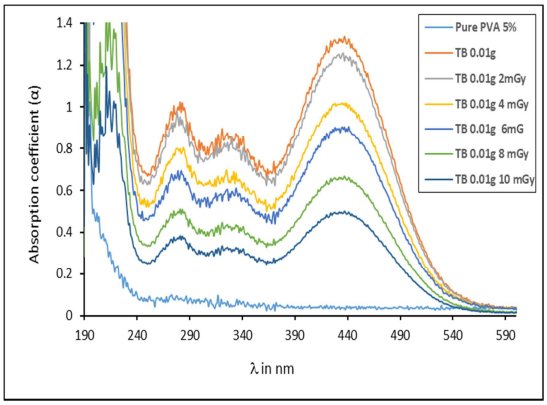

Figure 1: Shows the UV-visible spectrum with the absorption coefficient (α) at l = 435, 326 and 279 nm for (PVA 5%/TB 0.01 g) polymer composite film irradiated with 2 – 10 mGy.

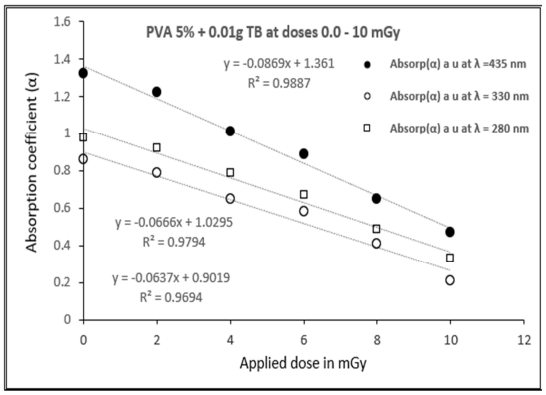

Figure 2: Shows the absorption coefficient of (PVA 5%/TB 0.01 g polymer composite films that give absorptions peaks at l= 435, 330 and 280 nm which were diminished following the radiation dose from 0 -10 mGy.

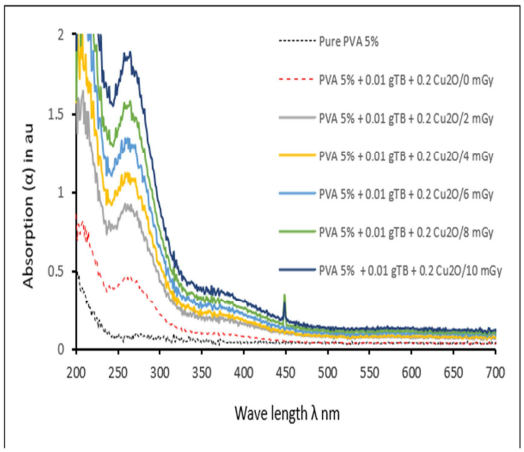

Figure 3: Shows the absorption coefficient of (PVA 5% + 0.01 TB + 0.2g Cu_2O) polymer composite films that give absorptions peak at l = 265 & 370 nm which were increases following the radiation dose from 0 -10 mGy.

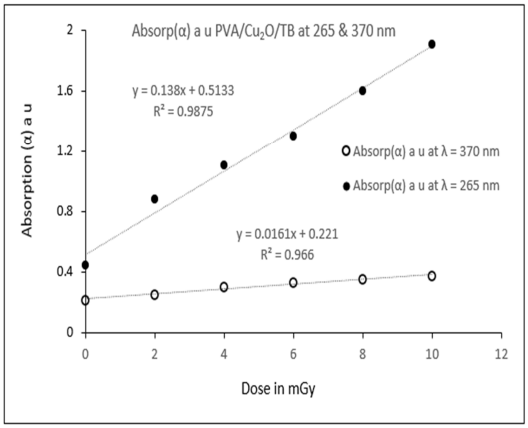

Figure 4: Shows the absorption coefficients (a) of PVA/Cu_2O/TB composite films at l = 265 & 370 nm versus the applied radiation doses 2-10 mGy.

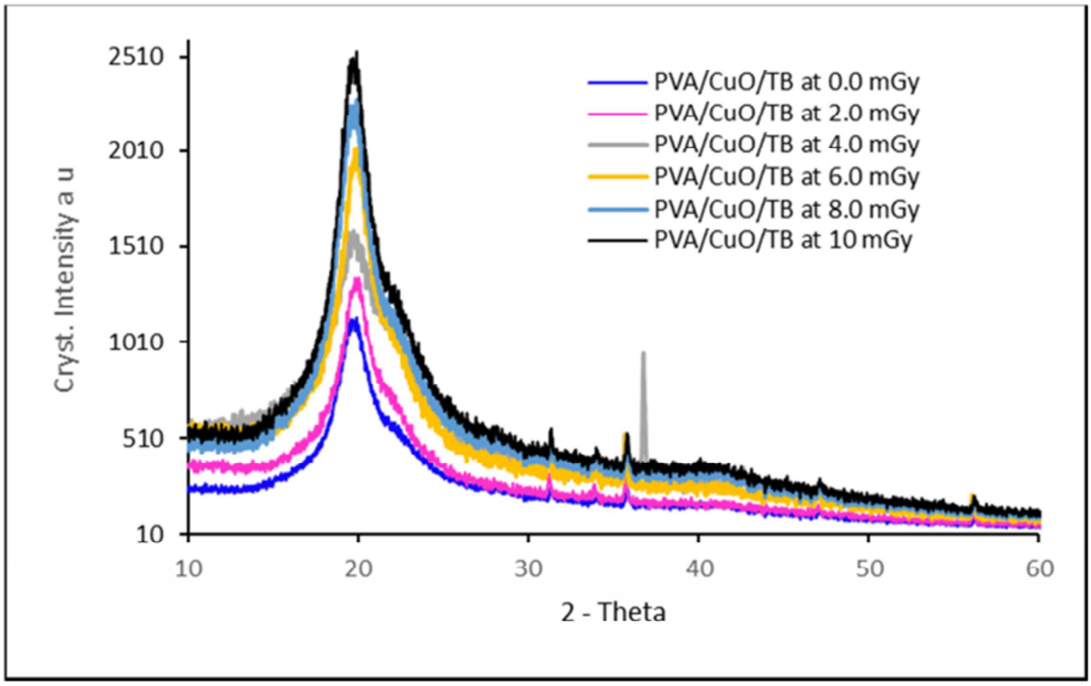

Figure 5: Shows XRD spectrum of the polymer composite films (PVA 5% mw/0.2 g Cu_2O/0.01 TB) after irradiation with doses range 0.0 – 10.0 mGy.

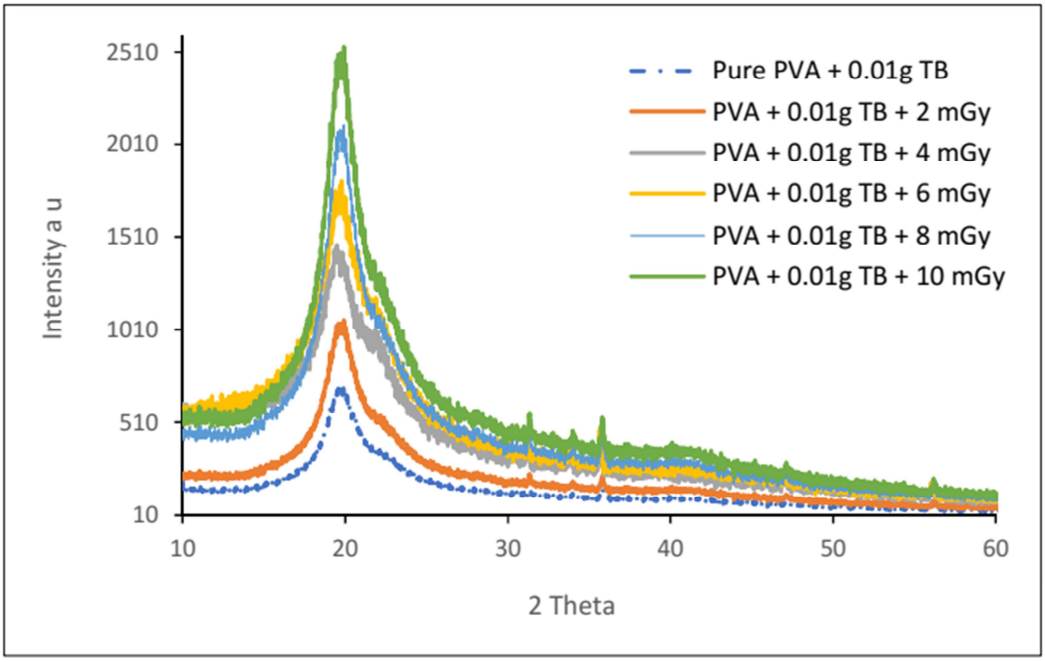

Figure 6: Shows XRD spectrum of the polymer composite (PVA 5% + 0.01 g TB) after irradiation with doses range 0.0 – 10.0 mGy.

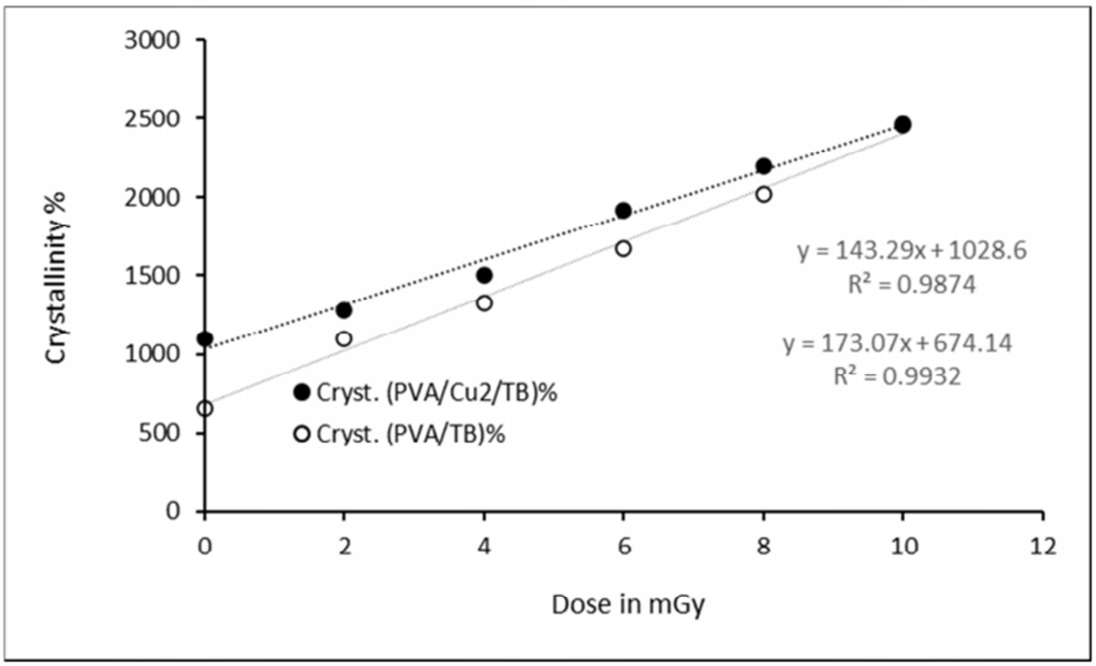

Figure 7: Growth of crystallinity% for both types of the film composites (PVA/Cu_2O/TB and PVA/TB) versus the applied radiation doses (0 – 10 mGy), indicating that: the crystallinity increases by 55.3% for (PVA/Cu_2O/TB) and 77.3% for (PVA/TB) which is near to the values calculated by Debye-Scherrer's equation i.e. calculation of area under the curve.

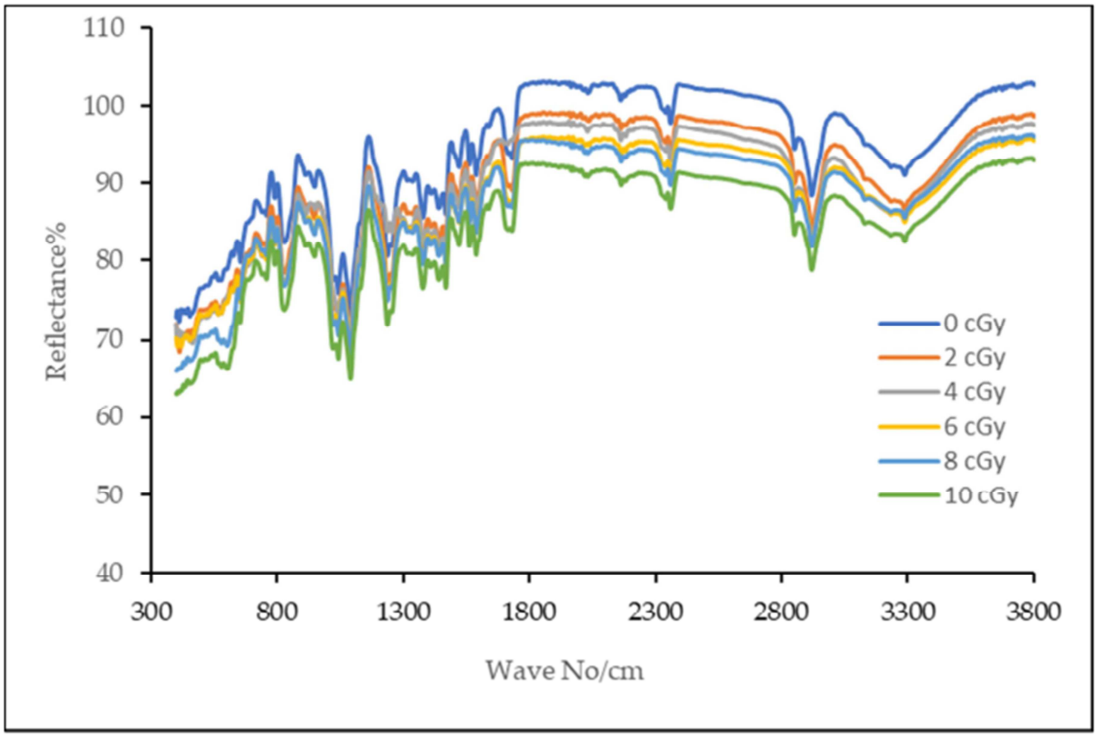

Figure 8: Shows the FT- IR spectrum for the PVA/Cu_2O/TB composite films receiving radiation doses from 0 – 10 mGy. Where the vibrational reflectance for molecular bonds being decreased following the radiation dose increment.

Table 1: FTIR molecular bond vibration and the relative functional groups in the composite polymer gel (PVA/TB)

FTIR Bands (cm^{-1})	Type of bond	Assignment
725.1 – 781.0	CH bending aromatic	TB backbone
883.2	C – C	PVA backbone
975.8	C – O stretch	TB - backbone
1062.7	C – O – C radiogenic	Polysaccharide's pyranose
1160.9	C – O	TB - backbone
1170.6	C – C	TB - backbone
1357.7	CH_2 wagging/rocking	PVA backbone
1623.8 - 1651	C = C alkenyl	TB - backbone
1633.4	δ O - H	non-bonded water
1681.6 - 1683.6	C = O amide	Carbonyl functional group
2125.1	C ≡ C alkenyl	Addition radiogenic bond
2879.2	CH_2 alkyl stretch	PVA backbone (Alkane)
3030.8	CH alkenyl	PVA backbone (Alkene)
3288	OH stretch vibration	PVA hydroxyl group

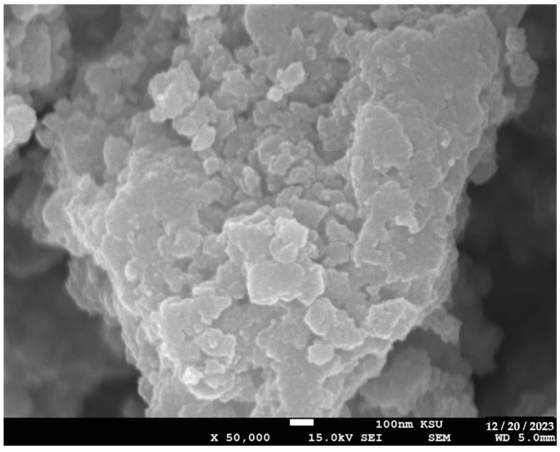

Figure 9: Shows the SEM for the PVA/Cu_2O/TB composite, presenting the cloudy nanocomposites of reduced Cuprous Oxide (Cu_2O) by irradiation to copper oxide (CuO).

3. Discussion

The UV-visible spectrum for the films consisting of PVA 5%/0.01 gram of Thymol blue composite showed three preeminent peaks of absorption coefficient (α) at λ = 435, 330, and 280 nm. However, these peaks decreased following the increment of radiation doses from 2 – 10 mGy (Fig. 1). These relative reductions in the absorption coefficient of the polymer composite films at λ = 435, 330 and 280 nm have significant (R^2 = 0.96) linear relationship with the amount of the applied radiation dose (Fig. 2) which is considered as one of the important properties of the dosimeter as well as a tissue equivalent and shaping [12]. The decreasing absorption could be ascribed to the induced bone session by irradiation [13]. However, such a fact could stimulate and encourage the applications of TB as a potential promising media for radiation detectors.

The PVA/Cu_2O/TB composite films present prominent absorption peaks at l = 260 & 370 nm i.e. in the range of ultraviolet radiation bands (Fig. 3). And is absorption band at visible light has been subtracted by the presence of TB absorption in the range of l = 390 – 490 nm that results in the appearance of semi-flat hum at λ = 355-400 nm. Unlike the case of PVA/TB films, these composites (PVA/Cu_2O/TB) show a linear increasing absorption coefficient following the applied radiation doses (2 – 10 mGy) (Fig. 4). The reduction of cuprous oxide (Cu_2O) to Cupric oxide (CuO) could explain the increasing absorption in the irradiated composite films. Such impressive phenomena could be utilizable and applicable for the benefits of ultraviolet radiation.

The XRD machine has been used to study the crystallinity of the compound. The diffracted radiation from the compound is used to discriminate between crystalline and non-crystalline materials [14, 15]. The degree of crystallinity can be calculated according to equation (1) given by Zhang et al. [16].

$$X_c = \frac{S_c}{S_c + S_a} \quad (1)$$

Where Xc is the approximation crystallinity percent, Sc is the total area of the diffracted peak and Sa is the area dispersion humps (the area of origin). From such context, the loss of crystallinity was 55.0% at a relative exposure of 10 mGy.

The x-ray diffraction spectrum for PVA/Cu_2O/TB composite film (Fig. 5) shows a prominent peak at 2 thetas = 19.5° which is an essence of PVA crystallinity as being confirmed by Tang et al, and Ricciardi et al, [17, 18]. Together with the structural orientation of PVA peaking at 2 thetas 31.3º, 34.2º and 35.8º (111). Same as in the case of PVA/TB composite films (Fig. 6). However, this crystallinity was increased by irradiation following the radiation doses increment from 2, to 10 mGy as shown in Fig. 7. Such increment of crystallinity could be ascribed to induced crosslinking by irradiation [19, 20]. The presence of reduced Cu_2O within the spectrum of XRD is seen with the prominent peak at 2 thetas 36.4º which is also, increased following the radiation doses. The FT- IR spectrum for the PVA/Cu_2O/TB composite film (Fig. 8) shows many vibrational

intensities; for instance, the vibrational band at 804 & 850 cm^{-1} referring to CH stretching of PVA backbone, 1063, 1096 cm^{-1} referring to C-O stretching vibration for PVA acetyl group. A vibrational at 1141 cm^{-1} refers to Polysaccharide's pyranose (C-O-C) within the composite. The vibrational band at 1352 cm^{-1} refers to extended (CH_2) rocking of the PVA backbone. The vibrational band at 1630 cm^{-1} refers to the bending vibration of the hydroxyl group (OH) for the PVA. The vibrational band at 1635 – 1698 cm^{-1} refers to the Carbonyl functional group (C=O) within the composite. The vibrational band at 2148, 2279 cm^{-1} refers to the Nitril group (C ≡ N) within the composite. The vibrational band at 2879, 3027 cm^{-1} refers to an extension of (C – H) of the PVA backbone (Alkane and Alkene respectively). The vibrational band at 3290 cm^{-1} is assigned to the true hydroxyl (OH) functional group as stated by some scholars [14, 21 - 26] and scheduled in Table (1). All the locations of the vibrational band showed either a blue or red shift due to the presence of reduced Cu_2O/TB that release surface plasmodium electrons.However, the image derived by the scanning electron microscope (Fig. 9) shows a cloud of nanoflakes of reduced Cupric Oxide with a morphologic size of 100 nm. Such morphological appearance agreed with the study highlighted by Azharudeen et al. [27]

4. Conclusions

The composite of PVA/TB could be used successfully in the detection of low radiation doses i.e. in the diagnostic range depending on the induced radiochemical action such as bleaching of color and the decreasing absorption occurs at λ = 435, 326, and 279 nm. Also, the composite of PVA/TB/Cu_2O could be used in the control of ultraviolet radiation level depending on the differential absorption in the range of λ = 265 & 370 nm.

Conflicts of Interest:

The authors declare no conflicts of interest.

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