Alteration in the optical, structural, and nuclear radiation attenuation characteristics of polyvinyl alcohol/lead oxide (PVA/PbO) films

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Abstract
The objective of this work was to perform a comprehensive analysis of the changes in the optical, structural, and nuclear radioactive attenuation properties of polyvinyl alcohol/lead oxide (PVA/PbO) films with different PbO contents (0.8, 1, 1.2, and 1.5 gm). The morphology of the prepared films was examined by scanning electron microscopy (SEM) and the results showed the homogeneous presence of PbO in the film image. Infrared spectroscopy (FT-IR) study indicates a significant decrease in the polyvinyl alcohol (PVA) peaks by increasing PbO contents. The presence of PbO in the prepared films was also confirmed by energy-dispersive X-ray spectroscopy (EDX). Practical and theoretical techniques were used to accurately analyze the gamma-ray attenuation properties of the PVA series. Using Linear Attenuation Coefficient (LAC) values other relevant parameters such as MAC were calculated. From the results, we found that 1.5% g PbO, had a higher density (2.54 g/cm3), and higher LAC, MAC, and lower Half Value Layer (HVL) values were observed. Moreover, the results of hardness experiments proved that the addition of PbO to a decrease in the flux.

Keywords: PVA/PbO films, FT-IR, EDX, Mass attenuation coefficient.

1. Introduction
Radiations are of a primary concern for the external exposure because of their high penetration power and domestic effects on humans. Accumulated doses from ionizing radiation can cause cancer, DNA mutations, sterility, etc. With the increased usage of radioactive materials in medicine and industry, the shielding is a priority in order to protect humans. A radiation shield is anything that creates a barrier between a human and a radiation source. The gamma shielding efficacy is described in terms of the half-value layer (HVL) or the mass attenuation coefficient [1,2]. These values for some common materials such as lead, iron, and concrete as a function of the energy of gamma rays and neutron particles are well known. The example of a widely used shielding material radiations is lead where, lead has a high atomic mass number and a high density. Lead (Pb) also is distinguished by its availability and low cost, as compared with other denser elements, but it has the disadvantage of having a low melting point. Iron is used in high and low energies. It is selected based on structural, temperature and economic considerations [3]. Concrete is a good attenuator of gamma rays as a shielding material and is a strong, inexpensive shield adaptable to different types of construction [2].

Polymer have numerous applications in various branches of the industry. One of the substances most used in the industry is polyvinyl alcohol (PVA). PVA is easily soluble in water and has been chosen as a host for dispersing metal-fillers [4]. The properties of PVA can be altered to produce significant structural strength, thus increasing the materials’ applicability and producing further progress in materials science [4]. Consequently, spread metal oxide particles have been used to create polymers with new mechanical, electrical and thermal properties according to various metals embedded in a polymer matrix.

As a result, the current study focuses on developing a highly transparent (PVA/PbO) type polymer system with high radiation attenuation properties. The study was also extended to include the dependence of some optical and mechanical properties on the lead oxide content in the prepared polymer samples.

2- Experiments methods:
2.1 Materials:
Poly (vinyl alcohol) (PVA) (C2H4O)n with a degree of polymerization (1700-1800) was used and was purchased from LobaChemie Pvt. Ltd. Lead monoxide (PbO) molecular weight 223 was purchased from Oxford Laboratory, Mumbai - India.

Scheme (1) PVA

2.2 Films preparation:
two samples of 10 wt% from PVA were prepared by completely dissolving in double- distilled water at temperature 85 °C, with continuous steering. A 1.5 g of PbO was mixed with one of the PVA solution with steering at 85 °C, then let to dried before used.
2.3 Characterization techniques:
Fourier transform infrared spectroscopy FTIR was conducted using FT-IR spectrosopy (ALPHA II, Bruker, Germany) at room temperature in the range 4000-400 cm\(^{-1}\). SEM images were recorded using BED-C 10.0KV, Jeol, equipped with EDX unit for analyzing the surface morphology. UV-Vis Spectrophotometer, Edinburgh Instruments high performance DS5 Dual Beam UV-Vis Spectrophotometer measures absorption and transmission as a function of wavelength for the wavelength range from 190 to 1100nm.

Linear attenuation coefficients for these samples were determined experimentally using a narrow, parallel, single-energy beam of emitted gamma rays. The linear attenuation coefficient of the standard lead oxide doped polymer was also determined by interpolation, to find an approximately suitable sample that could be used in radiotherapy protection. To prevent any scattered radiation from reaching the detector, an effective lead collimator is used. This lead scale is designed as one-piece 4cm long and 1mm diameter hole. The sample is placed halfway between the detector and gamma source. The incident radiation intensity and moved the gamma ray intensity (area under the peak) was measured at twelve positions for each sample to calculate the standard deviation which is an important indicator of the samples' homogeneity. This was done for energies of 1.333, 1.173 and 0.662 MeV using gamma sources of cobalt-60 and caesium-137, respectively. The detection system NaI (Tl) crystal as shown in Scheme 3.

By performing an X-ray diffraction investigation at room temperature with Cu Ka radiation at = 1.54 A (scintag, advanced diffraction system) with a nickel filter, spanning the range of 10-80, the amorphous nature of the materials were investigated. Density and Fourier Transform Infrared Spectroscopy were used to examine the impact of lead oxide on the polymer structure (FTIR).

The Archimedes technique was used to calculate the samples' densities \[ \rho = \frac{(W_{tp} - W_{tlq}) \times \rho_{lq}}{W_{tp}} \] (1)

Where \( W_{tp} \) is the weight of the polymer sample in air, \( W_{tlq} \) is the weight of the polymer sample in the immersion liquid, and \( \rho_{lq} \) is the density of the immersion liquid (Xylene = 0.863 gm/cm\(^3\)). \( \rho \) is the needed sample density. Additionally, the relation is used to compute the molar volume \( V = \frac{M_T}{\rho} \) (2) Where \( \rho \) is the density of the polymer sample and \( M_T \) is the total molecular weight of multi-component polymer system.

For specimen indentation, a typical microhardness tester (Leco AMH 100, USA) was utilised with a Vicker's diamond indenture. Glass test samples were indented using a weight of (100) grammes applied for 20 s. The microhardness of the investigated samples was assessed using polished samples in the form of plates that ranged in thickness from 3.5 to 5.6 mm. Each sample was exposed to five indentations at randomly chosen locations; as a result, the standard deviation of the measurement errors was determined to be roughly 4%. 

Scheme (3) Experimental arrangement
3. Results and discussion

3.1 Characterization of the function groups of the films:
FT-IR spectra of the pure blank PVA and (PVA/PbO) films were shown in Fig.1. In the present study, the FT-IR spectra of the pure blank PVA shows a band at 3,400 cm\(^{-1}\) due to the O–H stretching vibration band. Some broadness in OH, due to intermolecular hydrogen bonding between the hydroxyl groups, participated along the chains of the copolymer network structure. It was also found that a peak at 1,450 cm\(^{-1}\) was characteristic for symmetrical bending of C - H groups and a bands at 1,270 and 1,190 cm\(^{-1}\) due to C–O stretching coupled with O–H in plane bending. [5]. It is interesting to note that, the absorption peaks in the region 1,190–1,075 cm\(^{-1}\) corresponding to C–O stretching of hydroxyl groups was found to be disappeared for the (PVA/PbO) film [6]. The interaction between the PVA polymeric matrix and PbO possibly prevails in a physical manner, leads to the weakening of all bands of the blank PVA, due the interaction between PVA and PbO particles [7].

3.2 Scanning electron microscopy:
The SEM images shown in Figs.2 explain surface morphology of blank PVA and (PVA/PbO) films. It can be observed from the SEM images that, the blank PVA film image is observed as homogenous and smooth surface. On the other hand, the image of(PVA/PbO) film has a grains of PbO distributed homogeneously on the surface of PVA film [8].
3.3 EDX Measurements:
To determine the presence of the PbO in the (PVA/PbO) film, EDX analysis was carried out to be a supporting information confirming the presence of PbO in the PVA film. According to Fig. 3b, EDX analysis confirm the existence of PbO in the PVA film, while the EDX of the blank PVA film showed only the of presence of C and O atoms only [9].

Fig. (2) SEM of (a) blank PVA and (b) (PVA/PbO) films

Fig. (3) EDX of (a) blank PVA and (b) (PVA/PbO) films
3.4 Hardness and density measurement
Density and hardness are effective instruments for examining the structure and changes that have taken place in it because of compositional changes. They are sensitive to changes in the geometrical configuration, coordination number, cross-link density, and size of the interstitial gaps of (PVA) and (PVA/PbO) samples, as well as structural softness or compactness of the glass system. Fig. 4 depicts the composition of the current (PVA/PbO) as well as the experimental data for its density and hardness. It is clear from Fig. 4 that, blank PVA has lower values of density and hardness since when PbO is added to PVA, the density and hardness increase. The increase in density is due to the higher values of the molecular weight of PbO. The hardness results showed higher hardness values for samples containing PbO and this may be due to shortening of the bonds leading to more bond strength [10].

Fig. (4) The experimental values of density, and hardness of the prepared (PVA) and (PVA/PbO) Samples

3.5 Gamma ray attenuation coefficients
The experimental transmission and incident gamma ray intensity used to calculate the linear attenuation coefficient are shown in Fig. 5. As indicated in table 1, the observed mass and linear attenuation coefficients of (PVA/PbO) samples are helpful in the medical area. The information is helpful in domains like radiation dosimetry and others. It is vital to have a precise understanding of gamma ray photon attenuation and subsequent absorption in order to select the radiation to be administered without harming normal cells [11,12]. It is evident from this table that the attenuation coefficient rises as the weight fraction of PbO rises, which is due to the higher atomic number component Pb having a greater weight fraction than the PVA. According to Table 1, linear attenuation is preferable while utilizing low power. The observed incident and transmission gamma ray intensities were used to compute the mass attenuation coefficients. The mass attenuation coefficients increase with increasing concentrations of PbO at one energy and this is clear from this table, and this may be due to the increase in the values of its density and atomic number as well, thus the high percentage of PbO in these PVA films that participate in the structural chains of the polymer network helped to absorb gamma rays compared to other films, which leads to the fact that, the value of 1.5 of lead oxide is the best in attenuating gamma rays compared to other concentrations of lead oxide at different energies, and that the effectiveness of this shield is the highest possible at lower energies.

The thickness of the shield material known as the half-value layer (HVL), in which the incident radiation’s intensity is reduced to half of its original value. Fig.6 demonstrated that, the half-value layers of the (PVA/PbO) films under study at various energies reduced as the concentration of doped lead oxide increased and increased as the energy level rose. Due to the greater density of the (PVA/PbO) films, this may be ascribed to an increase in the mass attenuation coefficient. The synthesized PVA host polymer, which is doped with lead oxide at a content of 1.5, has greater shielding capabilities for this composition than some of the more well-known standard polymers, it may be inferred.
Fig. (5) Variation of transmission against thickness values of all (PVA/PbO) samples
As shown in the Fig. 5, the fraction of photons removed from gamma rays per unit thickness of PbO-free polymer material is displayed in that figure as an example. From the figure, it is clearly shown that the attenuation coefficient increase with the increase in the weight fraction of PbO which may be attributed to the increase in weight fraction of the higher atomic number constituent Pb as compared to other elements (C, O, H). The linear attenuation is better in lower energy than above, as shown in Fig. 5. The mass attenuation coefficients were calculated from the intensity of the measured incident gamma-rays and the intensity of transmittal gamma-rays [10].

Table 1 Linear attenuation coefficient $\mu$ (cm$^{-1}$) and mass attenuation coefficient $\mu/\rho$ (cm$^2$/g) of blank (PVA) and (PVA/PbO) absorber at Photon energies 0.662, 1.170 and 1.330 MeV.

<table>
<thead>
<tr>
<th>m$_{\text{PbO}}$ g/m$^2$</th>
<th>$\mu$ (cm$^{-1}$) 0.662 MeV</th>
<th>$\mu/\rho$ (cm$^2$/g) 0.662 MeV</th>
<th>$\mu$ (cm$^{-1}$) 1.170 MeV</th>
<th>$\mu/\rho$ (cm$^2$/g) 1.170 MeV</th>
<th>$\mu$ (cm$^{-1}$) 1.330 MeV</th>
<th>$\mu/\rho$ (cm$^2$/g) 1.330 MeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0594</td>
<td>0.0543</td>
<td>0.0449</td>
<td>0.079774</td>
<td>0.072925</td>
<td>0.060301</td>
</tr>
<tr>
<td>0.8</td>
<td>0.087</td>
<td>0.0614</td>
<td>0.0559</td>
<td>0.14616</td>
<td>0.103152</td>
<td>0.093912</td>
</tr>
<tr>
<td>1</td>
<td>0.164</td>
<td>0.1144</td>
<td>0.1042</td>
<td>0.33456</td>
<td>0.23376</td>
<td>0.212568</td>
</tr>
<tr>
<td>1.2</td>
<td>0.1676</td>
<td>0.1127</td>
<td>0.1026</td>
<td>0.382128</td>
<td>0.256956</td>
<td>0.233928</td>
</tr>
<tr>
<td>1.5</td>
<td>0.1698</td>
<td>0.1109</td>
<td>0.1011</td>
<td>0.431292</td>
<td>0.281686</td>
<td>0.256794</td>
</tr>
</tbody>
</table>

Fig. (6) Experimental values of half value layer (HVL) as function of blank (PVA) and different (PVA/PbO) Concentrations.

Conclusions
A comprehensive analysis of the changes in the structural and nuclear radiative attenuation properties of polyvinyl alcohol/lead oxide (PVA/PbO) films was conducted at different concentrations of PbO. The morphology of the prepared films was examined by scanning electron microscopy (SEM) and it was found homogeneous presence of PbO in the film image. Infrared (FT-IR) spectroscopy study indicated a significant decrease in the PVA peaks by adding the PbO. Also, energy dispersive X-ray spectroscopy (EDX) confirmed the presence of PbO in the prepared film compared to its absence in the blank (PVA) film. Practical techniques were used to accurately analyze the gamma-ray attenuation properties of the PVA series, at photon energies ranging from 662 to 1333 keV. Using LAC values other relevant parameters such as MAC were calculated. From the results, we found that 1.5 g PbO had a higher density (2.54 g/cm$^3$), higher LAC and MAC values and lower HVL values were observed. Moreover, the results of the hardness experiments proved that the addition of PbO increases the hardness of the polymer used in the study.

References
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