Preparation, morphological, and mechanical characterization of titanium dioxide (TiO2)/polyvinyl alcohol (PVA) composite for gamma-rays radiation shielding

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Abstract. Polyvinyl alcohol (PVA) has been prepared as a films with different volume ratios of titanium dioxide (TiO2). Atomic force microscope (AFM) was used to test morphology and grain size of the specimen surfaces. The results revealed that the surface roughness of specimen decreased with increasing the ratio of TiO2 whereas the grain size was increased. The stress-strain curves for TiO2/PVA composite films with 0%, 0.02%, 0.03%, and 0.04% TiO2 content are characterized. The mechanical performance of the TiO2/PVA composite films was clearly affected according to loaded TiO2 contrast to that of the pure film. Furthermore, the titanium dioxide (TiO2)/polyvinyl alcohol (PVA) composite samples examined as a shielding material of gamma ray. linear attenuation coefficient was measured by using the Cesium-137 (Cs-137) and gamma-ray photons 662 keV as a radioactive source. It was shown that the efficiency of shielding material increased with increasing the loaded amount of TiO2.

1 Introduction

The undesired hazards of X-rays, gamma-rays and neutron which cause great harm to nearby human being can be avoided by using several of shielding materials that have the ability to attenuate or absorb these types of radiations. Materials like lead and other high Z materials are used to attenuate this high-energy radiation. Although, high Z elements do not have the ability to block all types of radiations, especially neutron emissions in space or nuclear laboratories. They are some restricted in this materials applications because of their heavy weight, bulky space, and toxicity [1–3]. Therefore, the lightweight, workability, and its ability to attenuate the radiation, all this properties of filler-reinforced polymer composite which is non-toxic “lead-free” materials make it has a great public interest in many areas such as medical treatment, nuclear plant and mobile nuclear devices. For example, the mixing of ethylene-propylenediene rubber (EPDM)/low density polyethylene (LDPE) with boron carbide is used for neutron shielding widely [4], while in the shielding of against X-ray with the voltage range from 40 to 150 kV bismuth oxide (BiO) nanoparticles blended with polydimethylsiloxane (PDMS) is used [3]. This material is not suitable for a long-term use, because of their poor mechanical strength, low radiation resistance and thermal stability. Epoxy resin owing to containing rich hydrogen atoms are quite effective to decelerate fast and intermediate neutrons [5]. Moreover, the excellent mechanical properties which denoted by its superior solvent and chemical resistance, adhesive strength and good dimensional stability, there for epoxy-based composite for nuclear plants use is more suitable [6, 7]. Therefore, the matrix of epoxy composite that loaded with high concentrations of high-Z fillers is an attractive candidate, for radiation
shielding. Atactic material such as PVA has crystalline exhibits. In microstructure terms, the PVA composed mainly of 1,3-diol linkages [-CH2-CH(OH)-CH2-CH(OH)-] but a few percent of 1,2-diols [-CH2-CH(OH)-CH(OH)-CH2-] occur, this structure is depending on vinyl ester precursor conditions of polymerization [8]. Excellent film can be formed with polyvinyl alcohol has emulsifying and adhesive properties. This film has oil, grease and solvents resistance. It has high oxygen and aroma barrier, as well as high tensile strength and flexibility properties, all these properties are dependent on humidity. Higher humidity means more water is absorbed. The water will reduce the tensile strength, because the water acts as a plasticizer, but it will increase its elongation and tear strength. PVA has a melting point of 230 °C and 180–190 °C (356-374 degrees Fahrenheit) for the fully hydrolysed and partially hydrolysed grades, respectively [9-12]. The aim of present study is to prepare Polyvinyl alcohol (PVA) as a films with different volume ratios of titanium dioxide (TiO2) then, mechanical and morphological characterization will be investigated. The titanium dioxide (TiO2)/polyvinyl alcohol (PVA) composite samples examined as a shielding material of gamma ray

2 Experimental and Methodology

2.1 sample preparation

To prepare titanium dioxide (TiO2)/polyvinyl alcohol (PVA) composite sample, 0.25 g of PVA (provided by Sigma Aldrich) was dissolved in 15ml deionized water under constant stirrer for 2 hours at 90 °C. 50 mg/5ml titanium dioxide (5-10 nm, Anhui Elite Industrial Co., Ltd.) was dissolved in deionized water ultrasonically for 1 hour and three times repeated at 90 °C. The different volume percentages of ultrasonically titanium dioxide (0%, 0.02%, 0.03%, and 0.04%) was separately added into the constant polyvinyl alcohol solution. The vigorous mechanical stirrer was continued to ensure that the titanium dioxide particles were uniformly dispersed in a polyvinyl alcohol matrix. After that, the final mixture was poured into a petri dish and kept in the furnace for three days at 60 °C to remove the water. The obtained films have been cut to the required dimensions to conduct the tests of study.

2.2 Equipment’s and measurements

Atomic force microscope (AFM) (AA2000 Atomic Force Microscope, Angstrom Advanced Inc. with a high-Performance atomic-scale of resolution) was used to characterize the surface morphology and grain sizes of the (TiO2)/(PVA) films. The attenuation coefficient of gamma rays was measured by the scintillation detector (6S6P1.5VD, AL 35749, USA). this detector described as a positive high voltage utilizing Photomultiplier Tube (PMT) of a 1.5-inch and10 step linked to a NaI(Tl) (1.5“ X 1.5”) cylindrical scintillation crystal. The radioactive source used in this study is Cesium-137 (Cs-137) with radiation activity 0.8 mCi, half-life 30.17 years, and gamma-ray photons 662 KeV. For the purpose of measuring the linear attenuation coefficient of manufactured shields, the two lead collimators were used to obtain a good geometric arrangement of the system. These collimators have dimensions of (4 x 16 x 16 cm) and a central circular hole (1 cm diameter) to obtain parallel radiation. the distance between the detector and the radioactive source is 30 cm. figure 1 shows the geometric arrangement of the system.
2.3 Theoretical calculations

the fraction beam of gamma ray that is either scattered or absorbed due to interacting with the per unit thickness of a target material known as the linear attenuation coefficient (µ). Thus, the linear attenuation coefficient one of the most important parameters indicates that the penetration process of gamma rays throughout the shielding materials and depends on the incident photon energy and atomic number or effective atomic number of a target material. The interaction of gamma ray photons with a target material can expressed by the following [13]:

\[ I = I_0 e^{-\mu x} \]

(1)

Where, \( I_0 \) refers to the radiation that before passing through shielding material, \( I \) is the radiation that after passing through a thickness, \( x \) (cm), of shielding material. The thickness required to attenuate the radiation beam to half of what it was before passing through the absorbent material is known as a half-value layer (HVL). Thus, this is could be determined by the following relation [13]:

\[ HVL = \frac{\ln 2}{\mu} \]

(2)

Whereas the tenth value layer known as the thickness of a shielding material that required to reduce the incident intensity of gamma-ray photons to its tenth value at given energy [14]:

\[ TVL = \ln 10 / \mu \]

(3)

Also, the screening ratio, \( S \), represented by the following expressed [13]:

\[ S = \frac{I_x}{I_0} \times 100\% \]

(4)

The mean free path, \( \lambda_{mean} \), defined as
3 Results and discussion

3.1 Morphological analysis

In recent years, atomic force microscopy has been increasingly used to characterize the polymer structure [15], in which the preparation of samples didn't need any conductive layer that coated during an imaging process unlike SEM or staining in TEM, however, all its requirements are a sample surface without of scratches and undesired particles (dust and dirt). There are two modes that are performed by the atomic force microscope (AFM) the mode of contact and tapping. In our work, the contact mode was used to test morphology of the specimen surfaces. Figure 2 shows the AFM surface images of the prepared (TiO₂)/(PVA) films in 2 and 3-D.

![AFM Surface Images](image)

The evaluation of surface roughness parameters is very useful for several fundamental problems for example fraction, contact deformation, tightness and etc [16]. The roughness parameters of the (TiO₂)/(PVA) films are tabulated in Table 1. As can be seen, increase in the ratio of TiO₂ led to decrease in the surface roughness. It is observed that the surface pore size is strongly correlated with the surface roughness, i.e. the smaller the surface pore size the smoother the films surface and vice versa [17]. It may be suggesting that, the titanium dioxide (TiO₂) NPs with small diameters fill the gaps or holes between the protrusions of polymer and thus reduce the roughness of the film surface and get good surface finish.

![Table 1](image)

Table 1: The roughness parameters of the (TiO₂)/(PVA) films

| Sample       | Sₐ (nm) | Sₐ (nm) | Sₘₐ | Sₖₐ | Sₚ (nm) | Sₖ (nm) |
|--------------|---------|---------|------|------|---------|---------|
| 0% TiO₂/PVA  | 5.4     | 6.94    | 0.15 | 3.47 | 44.8    | 44.8    |
| 0.02% TiO₂/PVA| 3.84    | 5.6     | 1.24 | 7.6  | 45.9    | 45.2    |
| 0.03% TiO₂/PVA| 3.84    | 5.45    | 0.72 | 6.54 | 46.2    | 44.2    |
| 0.04% TiO₂/PVA| 3.44    | 4.45    | 0.62 | 4.11 | 40.7    | 40.1    |

* Sₐ: Roughness average; Sₐ: Root mean square; Sₘₐ: Surface skewness; Sₖₐ: Surface kurtosis; Sₚ: Peak-Peak; Sₖ: Ten point height.
the morphological analysis considered as useful tool to get information about grain size, grain boundary, pin holes, and surface uniformity[18-19]. In this study the surface roughness of prepared films was studied as a function of gray value. figure 3 shows the height cumulation distribution and roughness as a function of gray value. The height of grain size of films decreased with increasing the ratios of loaded titanium dioxide (TiO2) NPs. This result revel that the surface of films has a high smoothing feature.

The grain size is increased with increasing the ratios of the titanium dioxide (TiO2) NPs due to these films crystallinity is improved. figure 4 shows the granularity cumulation distribution and also the diameter of formed grains are listed in table. 2. The granular features of various scales exist in the film and are distributed almost evenly in some ranges. The film contains granules of different scales which distribute evenly in some arrays. Furthermore, the granular topographies have diverse irregular shapes, sizes and separations. Unclear aggregation was noticed in the sample.

Figure 3: shows the height cumulation distribution of (TiO2)/(PVA).

Figure 4: shows the granularity cumulation distribution of (TiO2)/(PVA).
Table 2: The diameter of formed grains

| Sample       | Avg. Size (nm²) | Avg. Height (nm) | Avg. Diameter (nm) |
|--------------|-----------------|------------------|--------------------|
| 0% TiO₂/PVA  | 20497.76        | 27.32            | 161.55             |
| 0.02% TiO₂/PVA | 43333.36        | 25.74            | 234.89             |
| 0.03% TiO₂/PVA | 23093.19        | 25.75            | 171.47             |
| 0.04% TiO₂/PVA | 22736.36        | 24.13            | 170.14             |

3.2 Mechanical properties

The study of the change in the polymeric dimensions as a function of stress is an important mechanical property of all polymers. Moreover, the nanoparticles that loaded in PVA chains, it is predictable to influence the mechanical properties. All samples of the prepared films were cut into strips of 10 mm wide and 20 mm long, for the tensile tests. The obtained results were summarized in table 3. the elastic modulus is determined from the slope of the linear part of the stress-strain curve, in addition, the yield and tensile strength as well. It was predictable that the mechanical effectiveness of the TiO₂/PVA composite films was significantly affected by dispersing TiO₂ nanoparticles into the PVA matrix. The stress-strain curves for TiO₂/PVA composite films with 0%, 0.02%, 0.03%, and 0.04% TiO₂ content are shown in figure 5. The mechanical performance of the TiO₂/PVA composite films was clearly affected according to loaded TiO₂ contrast to that of the pure film. The 0.02% TiO₂/PVA films offer decreased tensile strength, modulus, and elongation, compared to untreated PVA, while these parameters, started to increase at the ratios of 0.03%, and 0.04% TiO₂/PVA films. to understand systematically, the mechanical performance of TiO₂/PVA composite films depend on the loaded ratio of TiO₂ [20]. Therefore, when the TiO₂ content reached 0.02%, the tensile strength decreased as TiO₂ ratio was loaded. However, even when the TiO₂ adding exceeded 0.04%, the tensile strength was higher than that of the pure PVA matrix. In the TiO₂/PVA composite films, the hydrophilic PVA chains render to assist a comprehensive and whole hydrogen bonding network. The hydroxyl groups of PVA can serve on either hydrogen-bonding donors or acceptors. However, the covalent bonds in the PVA main chain make them a stronger, multivalent bridge compared to the separate hydroxyl groups [21].
Figure 5: The stress-strain curves for TiO$_2$/PVA composite films with 0%, 0.02%, 0.03%, and 0.04% TiO$_2$

Table 3: Summary of the tensile test results.

| Sample          | Elastic Modulus (MPa) | Tensile strength (MPa) | Elongation (%) | Yield strength (MPa) |
|-----------------|-----------------------|------------------------|----------------|---------------------|
| 0% TiO$_2$/PVA  | 6.09                  | 7.92                   | 602.22         | 2.87                |
| 0.02% TiO$_2$/PVA | 4.39                 | 7.78                   | 484.51         | 2.01                |
| 0.03% TiO$_2$/PVA | 5.23                 | 3.91                   | 538.72         | 2.35                |
| 0.04% TiO$_2$/PVA | 6.59                 | 8.68                   | 650.48         | 2.92                |

3.3. Shielding

In order to enhance the composed material that has shielding property, the amount of titanium dioxide was loaded into the PVA matrix through adding different volume ratios. Table 4. shows the values of linear attenuation coefficient, half-value layer and screening ratio of TiO$_2$/PVA which calculated according to the equations 1, 2, and 3 respectively. The relation between linear attenuation coefficient and TiO$_2$ ratio that is loaded into the PVA matrix illustrated in the figure 6. a. The linear attenuation coefficient is affected by a changing the concentration of loaded TiO$_2$. This suggests that the increase in the ratio of loaded material led to an increase in the absorption process of gamma-ray. Moreover, the increase in the absorption process attributed to the high distribution of the additive inside the base material. In general, the increase in density of shielding material will lead to an increase in gamma-ray attenuation. This result can give us the significant note that the polymer (PVA) alone is insufficient to
attenuate the gamma-ray photons. There is another way to demonstrate the performance of a linear attenuation coefficient of compounds by comparing the HVL values of the compounds. Figure 6.b shows that the half-thickness decreases with increasing loaded TiO$_2$. This is result refers to the fact that increasing the concentration of the additive improves the properties of the base material to attenuate the gamma-ray photons. So, this parameter will contribute to identifying the suitable thicknesses for shields.

![Figure 6](image1.png)

Figure 6: Shows the relation between: a. linear attenuation coefficient, b. half-value layer and c. screening ratio and TiO$_2$ ratio that is loaded in to PVA matrix.

Figure 7 shows the relation between thickness of a prepared samples versus the linear attenuation coefficient and half-value layer. It means that the linear attenuation coefficient and half-value layer increases and decreases when the thickness of the shield increases respectively.

![Figure 7](image2.png)

Figure 7: shows the relation between thickness of a prepared samples versus the linear attenuation coefficient and half-value layer.
Table 4. The values of linear attenuation coefficient, half-value layer and screening ratio of TiO$_2$/PVA

| Sample | Concentrations | Thickness (μm) | TVL (cm) | HLF (cm) | μ (l/cm) | S (%) | $\lambda_{mean}$ |
|--------|----------------|----------------|----------|----------|----------|-------|-----------------|
| 1      | PVA (pure)     | 10             | 25.10    | 7.56     | 0.091    | 0.009186 | 10.917          |
| 2      | PVA+0.02%TiO$_2$ | 8              | 24.49    | 7.38     | 0.094    | 0.007578 | 10.651          |
| 3      | PVA+0.03%TiO$_2$ | 3              | 24.09    | 7.26     | 0.095    | 0.002985 | 10.476          |
| 4      | PVA+0.04%TiO$_2$ | 9              | 23.51    | 7.08     | 0.098    | 0.008727 | 10.221          |
| A      | 1+2            | 18             | 23.84    | 7.18     | 0.096    | 0.019291 | 10.365          |
| B      | 1+2+3          | 21             | 23.33    | 7.03     | 0.098    | 0.020668 | 10.146          |
| C      | 1+2+3+4        | 30             | 21.40    | 6.45     | 0.107    | 0.032151 | 9.308           |

4 Conclusion

1. The polyvinyl alcohol (PVA) that contain different volume ratios of titanium dioxide (TiO$_2$) has been successfully prepared as films with a thickness of 10, 8, 3, 9 μm for 0%, 0.02%, 0.03%, 0.04% TiO$_2$ respectively.

2. The atomic force microscope (AFM) was used to test the morphology and grain size of the specimen surfaces. The average surface roughness of the specimens decreased according to increase the ratio of TiO$_2$ to be 5.4, 3.84, 3.84, 3.44 nm whereas the average grain size was increased to be 20497.76, 43333.36, 23093.19, 22736.36 nm$^2$ for 0%, 0.02%, 0.03%, 0.04% TiO$_2$ respectively.

3. The stress-strain curves for TiO$_2$/PVA composite films with 0%, 0.02%, 0.03%, and 0.04% TiO$_2$ content are characterized. Elastic Modulus, Tensile strength (MPa), Elongation (%), and Yield strength (MPa) was enhanced to be 6.59 MPa, 8.68 MPa, 650.48%, and 2.92 MPa respectively compared to pure film.

4. The titanium dioxide (TiO$_2$)/polyvinyl alcohol (PVA) composite samples examined as a shielding material of gamma ray. The linear attenuation coefficient was measured by using the Cesium-137 (Cs-137) and gamma-ray photons 662 KeV as a radioactive source. The linear attenuation coefficient was increased from 0.09160 for pure PVA to be 0.09783 for 0.04% TiO$_2$ while the HLF decreased from 7.5655 cm for pure PVA to be 7.0837 cm for 0.04% TiO$_2$. These results were shown that the efficiency of shielding material increased with increasing the loaded amount of TiO$_2$.

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