X-ray attenuation properties of PVDF-Bi_2O_3 composite thin films

Esther Lorrayne Machado Pereira[1,*], Adriana de Souza Medeiros Batista[1,2], Arno Heeren de Oliveira[1] & Luiz Oliveira de Faria[3]

[1] Departamento de Engenharia Nuclear, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brasil
[2] Departamento de Anatomia e Imagem, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brasil
[3] Centro de Desenvolvimento da Tecnologia Nuclear, Comissão Nacional de Energia Nuclear, Belo Horizonte, MG, Brasil

*E-mail: esther_machado@outlook.com.br

Abstract

Poly(vinylidene fluoride) (PVDF) is a linear semicrystalline homopolymer, and its polymeric chain is composed by the repetition of CH_2-CF_2 monomers. It is a material with many properties of industrial and biomedical interest has high mechanical performance and high resistance to exposure to ionizing radiation. Bismuth oxide (Bi_2O_3) is an interesting material characterized by X-ray shielding properties. Another very interesting feature is its non-toxicity, which makes it extensively incorporated into various products, such as cosmetics, biomaterials and medicines. In this work, we report an enhanced X-ray shielding effect related to adding Bi_2O_3 nanoparticles in PVDF matrix. The mass attenuation coefficients measured for nanocomposite made of PVDF filled with 50.0 wt % Bi_2O_3, were measured for energy photons in the range of diagnostic X-rays and compared with theoretical value, calculated by using the NIST photon cross section database. Composite characterization was performed with Field-emission electron microscopy (FE-SEM). The nanocomposite sample was radiographed and showed to be visible by the diagnostic technique, evidencing its attenuation property. The results imply that the effectiveness in shielding of X-ray is due to absorption capacity of Bi_2O_3 nanoparticles incorporated in PVDF, offering efficient protection against X-ray radiation for patients and devices in radiology procedures. It can also be used as an X-ray visible implant material.

Keywords: X-ray attenuation; PVDF; Bi_2O_3.

1.- INTRODUCTION

Polymeric biomaterials that have intrinsic radiopacity attracts considerable scientific attention. It is highly desirable as a post-implant visualization, as well as with embolization devices. However, polymeric materials are relatively transparent to X-rays, requiring the use of strategies for modifying them. In this case, the synthesis of polymeric biocomposites with the addition of an attenuating material X-rays becomes an alternative. These radiopaque additives are generally mineral compounds such as barium sulfate and bismuth oxide (Nottelet, Coudane and Vert, 2006). The incorporation of these additives also interferes with the physical, chemical and mechanical properties of the biocomposite.

Bismuth Oxide (Bi_2O_3) is an important semiconductor metal oxide, found in the form of a fine yellowish powderd in the market, which exhibits excellent optical and electrical characteristics, such as wide gap, high refractive index ($n\delta$ Bi_2O_3 = 2.9), high dielectric permittivity and good photoconductivity (Bedoya Hincapie *et al.*, 2012). In addition, it has high density, high melting point and high radiation resistance due to its high proportion of heavy atoms, thus enabling a high cross section. Yao *et al.* (2016) studied the attenuation properties of samples of concrete with the addition of Bi_2O_3 and with the addition of lead oxide (PbO). The sample containing 25% Bi_2O_3 showed higher linear attenuation coefficient and lower required thickness between concrete and Bi_2O_3 to block the same amount of radiation as PbO. It is also a less polluting option and does not compromise the structural capacity of the concrete.

The development of polymers loaded with metal oxides has been growing in order to take advantage of their potentially useful attenuating capabilities (Mccaffrey, Tessier and Shen 2012). Gershony *et al.* (2011) found that the junction of Bi_2O_3 and $BaSO_4$ resulted in a material with radiation attenuation capacity equivalent to a 0.5 mm thick lead plate, weighing 40% less. As it is a very dense material, it is suitable for absorbing high energy radiation such as X-rays and gamma rays. Bi_2O_3 is therefore an excellent candidate for high energy radiation protection, combining with the radio-resistance properties of PVDF homopolymer (Pereira, 2021).

2.- MATERIALS AND METHODS

The composites were produced through the solvent dissolution method using a powder-form PVDF matrix, supplied by Sigma-Auldrich, with density equivalent to 1.740 $g.cm^{-3}$, at 25 ^{o}C and corresponding average molecular weight at 534,000 $g.cm^{-1}$. Dimethylacetamide (DMAc) (3.0ml) and acetic anhydride (AA) (0.05ml) were used as solvent. The Bi_2O_3 is a nanostructured material (particle size 90-210 nm) with molecular weight equal to 465.96 $g.cm^{-1}$ and was supplied by Sigma-Aldrich. Bi_2O_3 dispersed in 1 ml of DMAc was added to the PVDF solution in the proportion of 50%, i.e. 1:1.

2.1.- Characterization by Field-emission Scanning Electron Microscopy (FE-SEM)

The microscopic images of this study were obtained in a scanning electron microscope with field effect emission (FEG-MEV) model SIGMA VP, manufactured by Carl Zeiss Microscopy. Two of the detectors available in the equipment were used: the Secondary Electron Detector (SE), which performs analysis of superficial regions, it is useful for topographic images, in high vacuum mode at working distances greater than 4 mm, and the Backscattered Electron Detector (BSE), which performs analysis in deeper regions of the sample, showing high sensitivity to differences in atomic number; the higher the atomic number, the brighter the material appears in the image.

The samples were prepared to perform this technique by covering with an ultra-thin layer of gold to prevent the accumulation of static electric fields in the material, due to electrical irradiation during image production, and to improve the final contrast of the image.

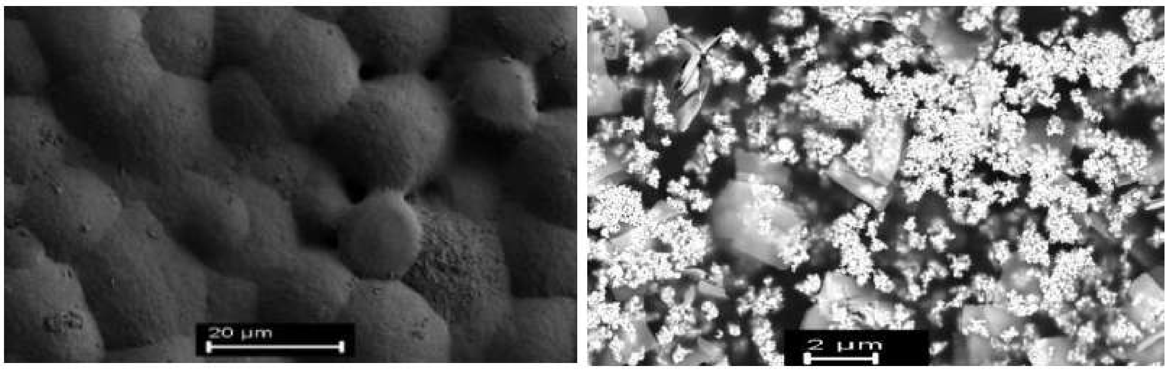
2.2.- Study of X-ray attenuation properties

X-ray attenuation tests were performed using the AMPTEK XR-100T-CdTe spectrometer for X-rays and gamma rays, and done with calibration on Ba-133, Co-57, Cd-109 and Am-241 radiation sources. However, only peaks with low uncertainty were used. After calibration, the spectrometer was aligned with GE industrial X-ray emission equipment, model ISOVOLT Titan E. For comparison purposes, measurements were taken without any attenuation and, later, with the sample to be tested. The instability of the radiation beam was verified through a monitoring camera, positioned at the exit of the radiation beam; however, the measured values were not used to perform any type of correction since the variation maximum found between irradiations was less than 0.5%. The calibration line that relates the channel used and the radiation energy has a linear correlation coefficient equal to 0.99999; this line was later used in the attenuation tests of the samples.

The X-ray visibility test was performed on an X-ray equipment diagnosis of VMI, Compacto Plus model, with radiography system computerized (CR), CR85-X image scanner and Drystar 5503 printer, both from AGFA. The following exposure parameters were tested: 117 kVp, 4 mA and 90 kVp, 2 mA (for contrast enhancement), at a distance of 1 m from the point focal length of the imaging plate. For assessing the ionizing-radiation visible implant composite, a phantom for attenuation measures in X-ray and fluoroscopy exams for control of quality, described ICRU (Report 48 Phantoms and Computational Models in Therapy, Diagnosis and Protection), was used simulating the abdomen region (Pereira, 2021).

3.- RESULTS

The SEM technique was chosen to observe the morphology and microstructure of the PVDF-Bi_2O_3 composite thin film. Figure 1 shows the formation of spherulites, characteristic structures of PVDF (Wisniewski *et al.* 2002). The presence of spherulites demonstrates that the dispersion of Bi_2O_3 does not affect the structural formation of the PVDF matrix after evaporation of the solvent, which can result in a sample with good dispersion. The proper dispersion of the charges favors the interaction between the composite components, combined with their properties. This good dispersion is confirmed in the image obtained using the BSE detector, in which Bi_2O_3 appears brighter than the polymer material. The image allows a more accurate visualization of Bi_2O_3 in relation to the polymer, showing a homogeneous dispersion, without formation of agglomerates.



a) b)

Figure 1.- SEM image of the PVDF/Bi_2O_3 thin film obtained with SE detector in (a) and obtained with BSE detector in (b).

3.1.- X-ray attenuation assessment

Figure 2 shows the spectrum obtained experimentally when irradiating the PVDF sample, compared to the X-ray spectrum emitted by the equipment, where characteristic peaks of type K of the Tungsten element (anode composition material) are observed, with energies corresponding to 57 .9 keV, 59.3 keV, 67.2 keV and 69 keV.

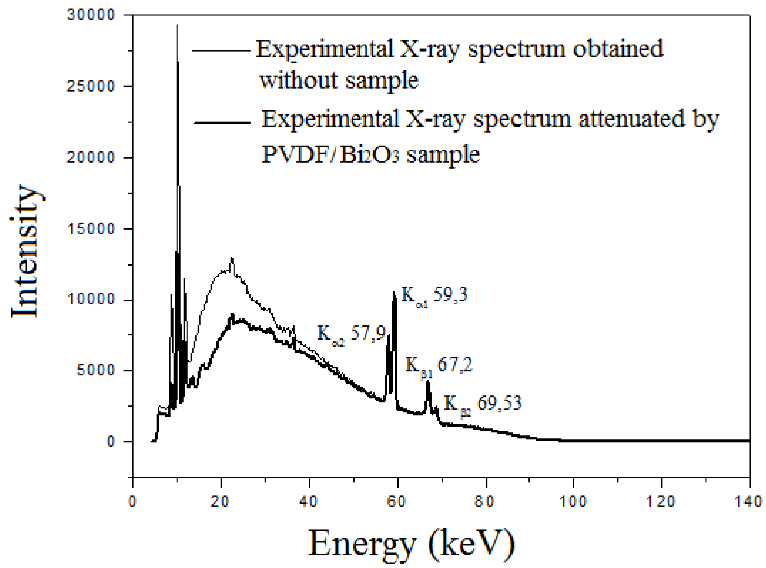


Figure 2.- Experimental X-ray spectra for evaluating the attenuation promoted by the $PVDF/Bi_2O_3$ sample.

The spectrum of the irradiated $PVDF/Bi_2O_3$ sample presents an intensity lower than that obtained without interposition of any sample to the detector, showing absorption by the composite of part of the radiation. To compare the predicted absorption by NIST for the composite of $PVDF/Bi_2O_3$ with the experimental data, the absorption coefficient was calculated. The mass attenuation coefficient is defined as the ratio of the linear attenuation coefficient (in cm^{-1}) to the absorber density (in $g{\cdot}cm^{-3}$). As μ/ρ is often expressed in cm^2/g, the attenuation of X-rays by any material can be demonstrated as a function of this coefficient using the following equation:

$$I = I_0 e^{-\langle \mu | \rho \rangle \rho x} \tag{1}$$

Where I_0 and I are the intensities of incident X-rays and transmitted beams, respectively, and x is the thickness of the material. Through equation 1 it is possible to determine the linear attenuation coefficient:

$$\mu = -\frac{1}{x} ln\langle I | I_0 \rangle \tag{2}$$

The density of a PVDF matrix composite filled with Bi_2O_3, such as the one in the present study, is calculated in terms of volume fraction as:

$$\rho_{composite} = \rho_{PVDF} . \omega_{PVDF} + \rho_{Bi_2O_3} . \omega_{Bu_2O_3} \quad (3)$$

Figure 3 presents a graph that demonstrates the similarity in the pattern of energy distribution by absorption coefficient between the data predicted by NIST and the experimental data. The agreement observed between experimental and theoretical data demonstrates the achievement of an attenuator composite that adequately combines the properties of PVDF matrix and Bi_2O_3. Table 1 shows the percentage of X-ray attenuation using 523 counting points and taking into account the attenuation data between 1 keV and 100 keV, using the equation:

$$At\% = 1 - \frac{I}{I_0} . 100 \quad (4)$$

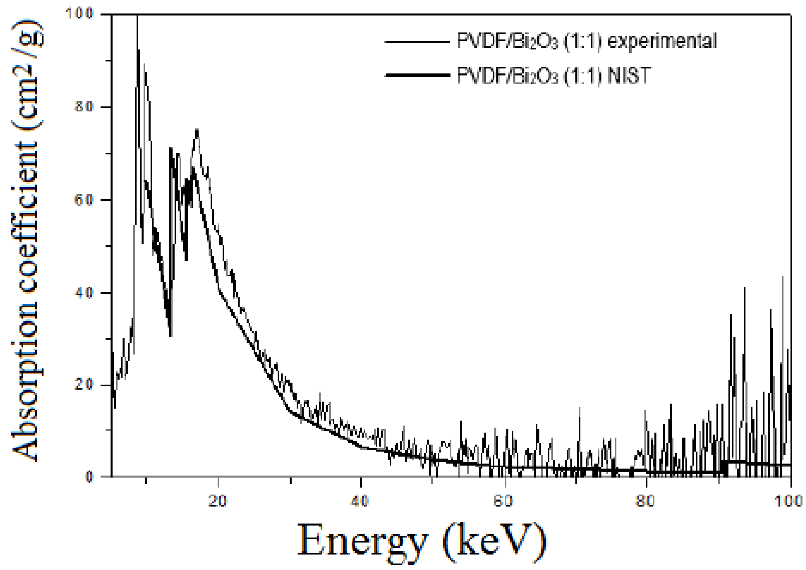


Figure 3.- Comparison between NIST predicted attenuation and experimental attenuation for the PVDF/Bi_2O_3 sample.

Table 1.- Percentage of total X-ray attenuation by PVDF/Bi_2O_3 sample.

Average	Standard deviation [$SD\pm$]	Standard Error [$SE\pm$]	Number of Counting Points
19,35946	52,32201	2,28788	523

X-rays of the sample irradiated in medical equipment confirm its attenuation capacity, as it appears visible on the radiographic image.

3.2.- X-ray images of the PVDF/Bi_2O_3 sample

Figure 4 a) shows an X-ray image of the PVDF/Bi_2O_3 sample positioned on top of a 1 cm acrylic plate obtained using the exposure parameters of 117 kVp and 4 mA. Figure 4 b) shows an X-ray image of the same sample irradiated under the same exposure parameters, but positioned in the body simulator for the abdomen region. To increase the contrast between the simulator and the composite samples, new exposure parameters with voltage reduction (90 kVp) and current increase (2 mA) were used (Figure 4 c)).

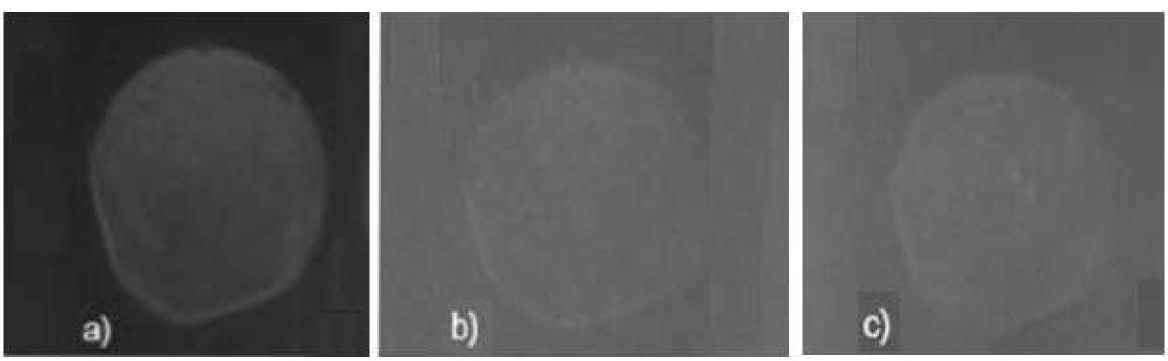


Figure 4.- X-ray images of the PVDF/Bi_2O_3 sample taken at different exposures.

The possibility of viewing samples when exposed to X-r7ays confirms their attenuating potential. The image obtained with the sample positioned inside a body simulator demonstrates its potential for use as a visible implant by the diagnostic technique.

4.- DISCUSSION

Polymeric materials have attractive mechanical properties for use in engineering, such as plasticity and lightness. It is also possible to add characteristic properties of other types of materials by producing a composite. For this work, it was sought the synthesis of a material that presented X-ray attenuating properties, flexibility and lightness for medical and engineering use. Bismuth oxide is known to be an attenuating material and the aim of this work was to make the most of this property, even when in conjunction with a polymeric material. Therefore, NIST's theoretical data was used to verify if the predicted properties of the PVDF/Bi_2O_3 thin film were experimentally achieved. This is because the synthesis process can interfere with the final property of the composite. By observing the similarity between the final attenuation behavior of the composite and that theoretically predicted by its composition, it was ensured an effective synthesis process. PVDF is a polymer that has important mechanical and radioresistant properties, also contributing to the final characteristics of the composite.

5.- CONCLUSIONS

PVDF/Bi_2O_3 samples were prepared with proportional addition of 50% of the metal oxide in relation to the polymer mass. Attenuation tests were carried out and the resulting spectrum showed the absorption suffered by the composite of part of the radiation. When compared to the absorption predicted by NIST, the PVDF/Bi_2O_3 (1:1) composite showed similarity in the pattern of energy distribution by absorption coefficient. X-ray images were obtained and demonstrated that the attenuation properties of composites allow their visualization by this diagnostic technique. SEM images demonstrate that Bi_2O_3 dispersion in the matrix does not harm the PVDF structure.

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