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Radiation shielding with Bi_2O_3 and ZrO_2:Y composites: preparation and characterization

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ABSTRACT

Despite the benefits of medical imaging examinations, there is a worrying contribution of dose of radiation to population due to the high dose procedures. Procedures as interventional radiology, Computed Tomography (CT) and nuclear medicine provide high doses to the skin of patients, provoking radiation deleterious effects. New attenuators materials have been widely investigated for radiation shielding in those regions of high risk, allowing significant dose reduction near the patient's skin. Composites with Bi_2O_3 and ZrO_2:Y metals were obtained by mixing them with P(VDF-TrFe) copolymers from casting. Composites were produced with concentrations of 2, 4 and 8% wt. of Yttrium stabilized zirconia. Bi_2O_3 containing composites were produced with the same concentrations (2, 4 and 8% wt.), with Bi_2O_3 particles being previously functionalized with methacrylic acid (MAA). The composites were characterized by FTIR. The entrance skin dose characterization was performed with and without the use of radiation protective shielding. The composite samples were exposed to an absorbed dose of 100 mGy of RQR5 beam quality (70 kV X-ray beam). The attenuation factors, evaluated by XR-QA2 radiochromic films, indicate that both P(VDF-TrFE)/Bi_2O_3 and P(VDF-TrFE)/ZrO_2:Y composites are good candidates for use as patient radiation shielding in high dose medical procedures.

1. INTRODUCTION

Medical radiology offers great benefit to patients. However, the radiation contributes for the workers and individuals exposure, significantly increasing dose to population [1]. Annually, specifics high dose procedures as interventional fluoroscopy, Computed Tomography (CT) and nuclear medicine make up a small percent of the imaging procedures in many countries in Europe and in the United States [2]. However, these procedures are responsible for 78-89% of the total yearly exposure to radiation from medical imaging. All interventional procedures contribute to the total collective effective dose in the range of 3.5-14 mSv for Europe and 2-20 mSv for UK, while, CT contribute up to 50% of the collective radiation dose from all radiographic examinations [3,4].

In order to minimize the deleterious effects of radiation exposure in specifics high dose procedures, there is an increasing interest for the development of new attenuator materials

[5,6]. These materials may shield part of the radiation beam, decreasing doses in regions of high risk. In this context, composite materials containing compounds or elements such as barium sulfate, copper, gadolinium, gold, lead, molybdenum, rhodium, silver, tungsten, bismuth, zirconium oxide, iron oxide and zinc have been studied elsewhere. Nowadays, composites containing bismuth are widely applied as protective shielding in radiological CT scans.[7,8]

Zirconium is the 18^{th} most abundant element on Earth. It occurs in nature as the free oxide ZrO_2. In addition, it has excellent mass attenuation coefficient and other properties such as high strength, high fracture toughness, excellent wear resistance, high hardness, excellent chemical resistance, good oxygen conductivity and piezoelectric, pyroelectric and dielectric properties [9,10]. In general, the polymorphism of zirconium can be tuned by cation doping as yttrium (Y^{3+}) that is widely used as a stabilizer of the tetragonal phase. Besides it improves the mechanical strength and thermal stability of ZrO_2. [11,12]

In this work, composites containing zirconia and bismuth oxide were studied aiming application as attenuating materials in high dose medical procedures. Several studies of composite materials based on a polymer matrix and metal filler include different methods to preparation. Polymers are lightweight, conformable, flexible, and easy to process materials. Due to these properties, polymeric based mixtures are ideal candidates to produce thin and lightweight composites required to this application. Synthesis *in situ* polymerization, sol-gel methods and *in situ* emulsion polymerization have been used to prepare composites with zirconia as filler material [13, 14, 15]. In general, polymerization of monomers and formation of inorganic particles are made separately. After this first step, composites are produced by mechanically mixing polymer with a metal material. Organic acids have been utilized to improve the compatibility, rendering additional reactivity between metals and the organic matrix. The surface modifiers using methacrylate groups make the particles polymerizable in radical polymerization [16, 17].

Thus, in this study, we investigated the radiation shielding properties of composites made of inorganic material as filler, by a sol–gel method, in poly(vinilidene fluoride-tryfluorethylene) [P(VDF-TrFE] copolymers that are used as the polymeric matrix. Two different metal attenuators were used as fillers: zirconia stabilized by yttria (8% wt.) and bismuth oxide. Both metallic oxides were surface-modified by methacrylic acid (MAA or MAc), $C_4H_6O_2$. The composites were characterized by fourier-transform infrared spectroscopy (FTIR), in order to detect the appearing and/or extinction of chemical bonds, and UV-Vis spectrophotometry, in order to measure the sample optical transparence.

The effective attenuation factor of P(VDF-TrFE) composites for different concentrations of ZrO_2:8%Y_2O_3 and Bi_2O_3 are investigated. Radiation shielding characterization was performed by sandwiching P(VDF-TrFE) based composite film between two external layers of XR-QA2 radiochromic films. In this setup, one layer is directly exposed to the X-rays beam and the other measures the attenuated beam. The study will be focused in the shielding of X ray radiation energies most commonly used in high dose radiology procedures.

2. MATERIALS AND METHODS

2.1. Preparation of composites

The synthesis of the composites involves the dispersion of metal particles in the P (VDF-TrFE) host matrix in various concentrations under magnetic stirring. The composites films were produced from *casting*.

2.1.1 P(VDF-TrFE)/(Bi_2O_3 /MAA)

Polymer based composites having methacrylic acid (MAA) functionalized Bi_2O_3 microparticles as the filler material were prepared with 10:1 concentration. Poly(vinylidene fluoride – trifluorethylene) copolymers [$P(VDF\text{-}TrFE)_{50/50}$] was dissolved in DMAc (n,n-dimethylacetamide). Surface-modified Bi_2O_3 microparticles were added to the solution with concentrations of 2, 4, 8 %wt. Semi-transparent films were obtained after solvent evaporation at 60°C.

2.1.2 P(VDF-TrFE)/(ZrO_2:8 at.%Y)

Poly(vinylidene fluoride – trifluorethylene) copolymers [$P(VDF\text{-}TrFE)_{49/50}$] was dissolved in DMAc (n,n-dimethylacetamide). Zirconia stabilized by yttria (ZrO_2:8%Y_2O_3) microparticles were dispersed into concentrations of 2, 4 and 8 %wt of copolymer matrix under sonication to form a suspension. After solvent evaporation at 60°C, this process produced semi-transparent films of c.a. 50 μm, as seen in Figure 1.

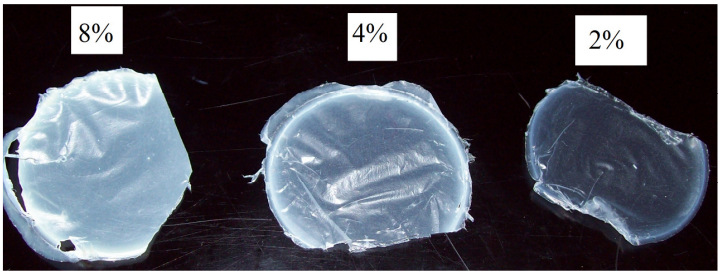


Figure 1: P(VDF-TrFE)/ZrO_2 :Y_2O_3 composites films with concentrations of 2, 4 and 8 %wt of ZrO_2 produced by casting from DMAc.

2.2. Material characterization

The composites characterization was made by fourier-transform infrared spectroscopy (FTIR). The FTIR spectra, collected with 32 scans each, were measured at a BOMEM 100 spectrometer for wavenumbers ranging from 200 to 4000 cm^{-1}. The composites were characterized by fourier-transform infrared spectroscopy (FTIR), in order to detect the appearing and/or extinction of chemical bonds.

2.3. Irradiation setup

The radiochromic films are sensitive for doses ranging from 0.1 to 20cGy and they have the same response for X-rays effective energies ranging from 20 to 100 keV. In addition, they have a good uniformity in the color indices distribution even when the ROI (region on interest) is changed. It is also possible to use high spatial resolution during film scanning. However, many factors may result in fluctuations in color intensity, such as defects in film structure such as the optical structure of the film's active layer, defects in film structure, scratches and external agents. [18,19]

Thus, special care was required when handling the radiochromic films before and after the irradiation and scanning processes. The composites films were sandwiched between two XR-QA2 Gafchromic® radiochromic films. In this setup, one radiochromic film is directly exposed to the x-rays beam and another one measures the attenuated beam.

After storing the XR-QA2 films for 24 hours at room temperature under no light conditions, the composite samples and the XR-QA2 films were exposed to an absorbed dose of 10 mGy of RQR5 beam quality (70 kV X-ray beam). The irradiated radiochromic films were scanned under the same conditions in order to obtain a more reliable result. All films were scanned using the same size ROI in high resolution mode and saved as tagged image file format (TIFF).

The free software Image J® was used to evaluate the color intensities used in the construction of the calibration curve of XR-QA2 Gafchromic® radiochromic films. By this program, was selected the same reading size area in all films. Among the RGB components, the red color intensity has presented the best resolution. Furthermore, was considered the average optical density taken over the selected area.

3. RESULTS AND DISCUSSION

3.1 Characterization of materials

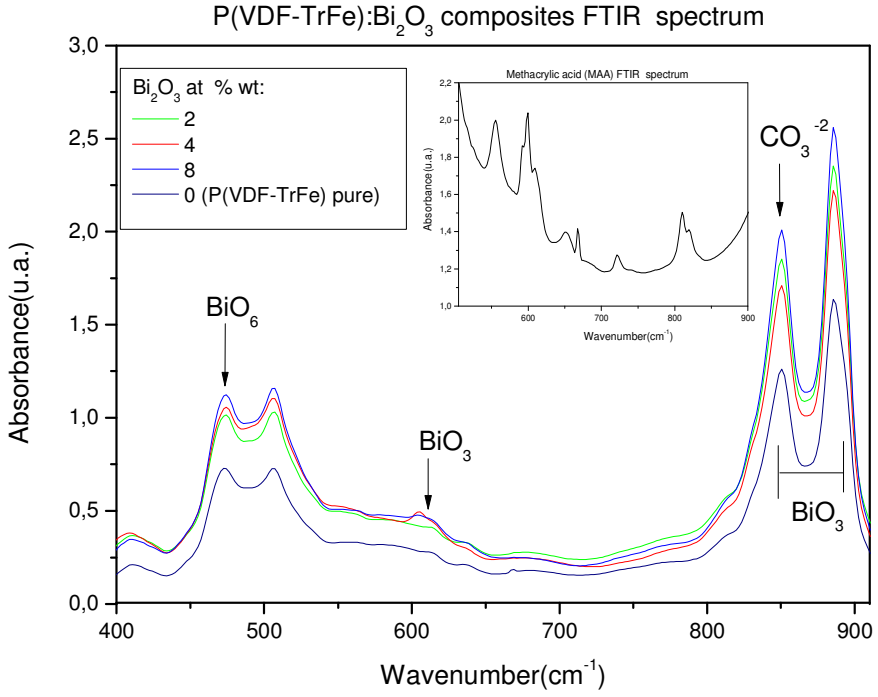
3.1.1 FTIR spectra of P(VDF-TrFE)/(Bi_2O_3/MAA) composites

The polymorphic forms of Bi_2O_3 have been widely studied. They can crystallize in six forms: α (monoclinic), β (tetragonal), γ (body-centered cubic) and δ (face-centered cubic), tetragonal ε-phase, and triclinic ω-phase. The α -phase is the most stable phase at room temperature, leading to high applicability in superconductors syntheses, ferroelectric compounds and photocatalysts systems. On the hand, the δ -phase is the stable phase at high temperatures (730–824ºC). It has technological applications because of its high oxygen ionic conductivity. The electronic structure of Bi^{3+} is characterized by the presence of $6s^2$ pair electrons, leading to high polarisability of the cation lattice, oxide ion mobility and the ability of the Bi^{3+} to accommodate highly disordered surroundings, resulting in vacancies of a quarter of the oxygen sites in the fluorite-type lattice. [20]

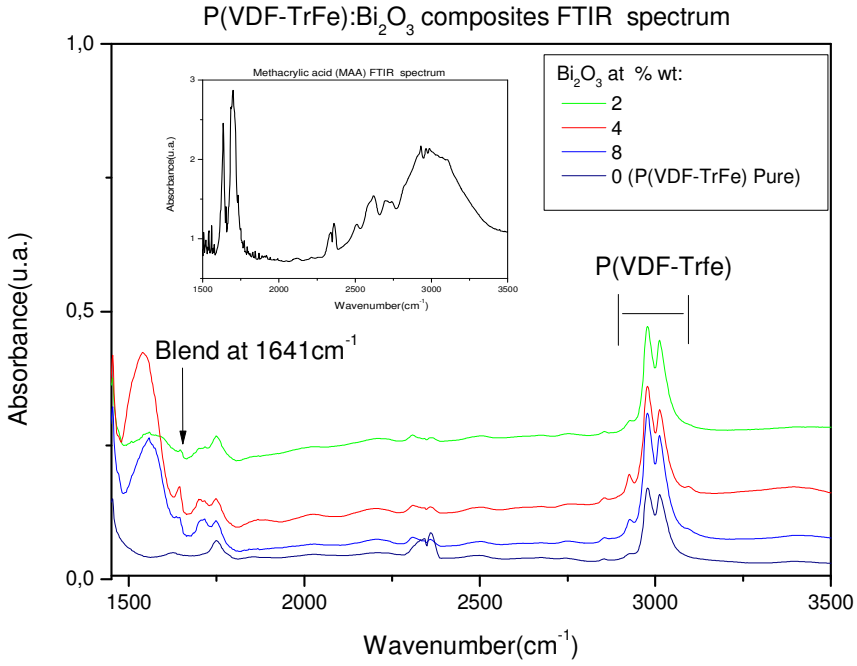
The FTIR spectra for composites at 0, 2, 4 and 8 %wt of Bi_2O_3 in the 400-900 cm^{-1} range is shown in Figure 2(a). The metal-oxygen (Bi-O) vibration correspond to bands around 700 ~ 400 cm^{-1}. The absorption band at 470 cm^{-1} can be attributed to doubly degenerate bending vibrations of [BiO_6] units. Otherwise, the absorption band at 610 cm^{-1} is attributed to the vibrations of Bi-O bonds in BiO_3 units. The band at 840-880 cm^{-1} band is characteristic of Bi-

O stretching vibrations of BiO_3 units.[21] FTIR data analyses indicate the coexistence of BiO_3 and BiO_6 groups, which could result in an increase of the covalent bonding between bismuth and oxygen. It is possible due to a connection through atoms of oxygen by continuous network of octahedral [BiO_6] groups and the high polarizability of Bi^{3+} cations. Furthermore, the absorption band at 850cm^{-1} can be attributed to v_2 and v_3 mode vibration modes of CO_3^{-2} group that is present in the residual carbonate when using $Bi_2O_2CO_3$ as a precursor. However, the bands at 472 and 506cm^{-1} are well known to be attributed to the ferroelectric β-phase of the PVDF homopolymer and also to the ferroelectric of P(VDF-TrFE)$_{50/50}$. Because of the proximity of the 470 cm^{-1} and 472 cm^{-1}, a more detailed investigation is need to elucidate the attribution of these bands. In Fig. 2 (a) the transmittance FTIR spectrum of pure Methacrylic acid (MAA) is also presented in the inset for comparison purposes. The band at 888 cm^{-1} is also attributed to P(VDF-TrFE) copolymer, i.e. the rocking and symmetric vibrations modes of CF_2 molecules. [22]

The FTIR spectra for composites at 0, 2, 4 and 8 %wt of Bi_2O_3 in the 1400-3500 cm^{-1} range is presented in Fig.2(b). P(VDF-TrFe) active modes in infrared are observed at 3012 cm^{-1} and 2977 cm^{-1} bands corresponding to antisymmetric ν_a (CH2) and symmetric ν_s (CH2) stretching, respectively. The increasing absorption bands at 1645 and 1730 cm^{-1} are attributed to MMA, as it can be seen in the inset of Fig. 2(b). It was remarked that Faria, L. O. and Moreira, R. L., (2000) [23] have observed an absorption band at 1643cm^{-1} in P(VDF-TrFE)/PMMA blends which is active only for the mixtures. This absorption band is clearly an experimental evidence of the strong interaction between the copolymer and the PMMA chains. Thus, this could be an alternative explanation for the band at 1645 cm^{-1}.



(a)



(b)

Figure 2: FT-IR spectrum of P(VDF-TrFE)/Bi_2O_3 composites films with concentrations of 0, 2, 4 and 8 %wt of Bi_2O_3 at 400-920 cm^{-1} (a) and 1400-3500 cm^{-1} (b) range.

3.1.2 FTIR spectra of P(VDF-TrFE)/ZrO_2:8%Y_2O_3 composites

In this section it is described the investigations about the P(VDF-TrFE)/ZrO_2 composites using zirconia stabilized by yttria (ZrO_2:8%Y_2O_3) microparticles at concentrations at 0, 2, 4, 8 %wt. The FTIR spectra are shown in Fig. 3. of the composite P(VDF-TrFE)/ZrO_2:Y_2O_3 at 8%, whose fill material is zirconia stabilized by yttria. Figure 4 displays the measured by the FTIR spectrum where can be observed 667cm^{-1} and 722cm^{-1} bands that are associated with YO_2 s-stretch and Yttrium oxide (Y_2O_3), respectively. The bands at 471 and 744 cm^{-1} can be attributed to zirconium oxide. The β phase of P(VDF-TrFE) is also show at 472 and 506, 851 and 886cm^{-1} bands correspondent at w (CF2) and δ (CF2), νs (CF2) and r(CF2), r(CF2) and νs (CF2), vibrational modes, respectively. However there was some saturation in the signal measured on some band range, which can be related to the thin film thickness of the composite, the same happened in the other sample.

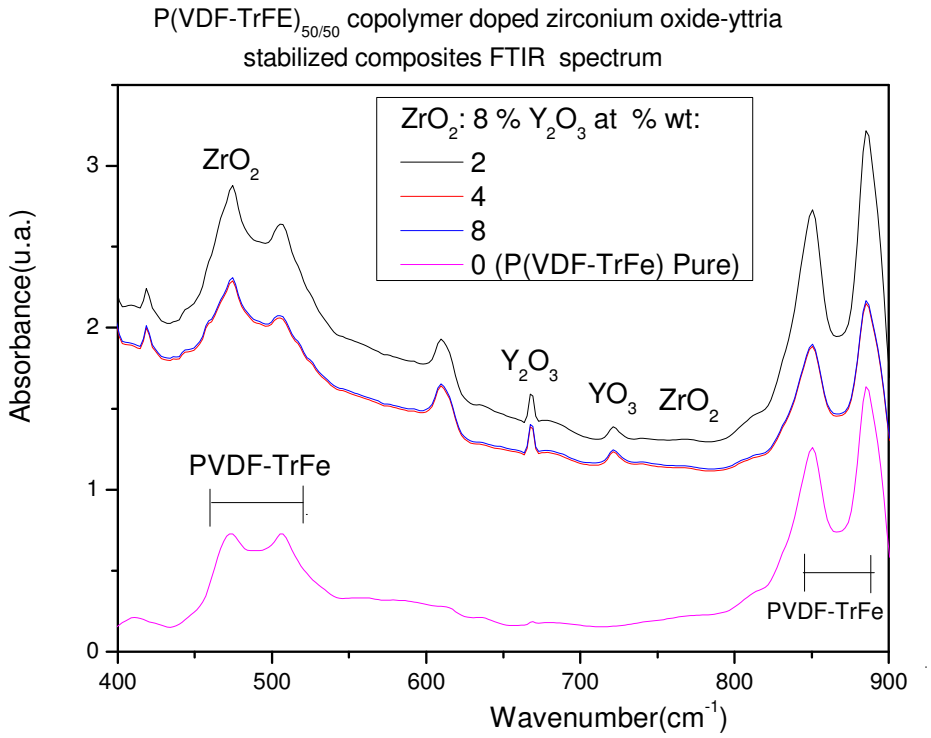


Figure 3: FTIR spectrum of the P(VDF-TrFE)/ZrO_2:8%Y_2O_3 composites films.

3.2 Radiation Shielding

The radiation qualities applied to measurements in the radiation beam as emerging from X-ray source assembly, are setting for each tube voltage (kV) with an adjust total filtration, considered the specifics half-value layer and homogeneity coefficient. In Table 1 has the characterization of standard radiation qualities used in this work, according to standard IEC61267:2005. [24]

Table 1. Characterization of Standard Radiation Qualities (Source: IEC61267:2005)

Standard Radiation Quality	X-Ray Tube Voltage (kV)	First Half-Value Layer (mm of Al)	Homogeneity Coefficient
RQR2	40	1.42	0.81
RQR5	70	2.58	0.71

The more common quality beams used for conventional radiology and interventional radiology are RQR5, RQR8 and RQR9. However the RQR5 is somehow adopted elsewhere as a kind of reference. Then, although the XR-QA2 Gafchromic® radiochromic films are reported to have the same response for effective energies ranging from 20 to 100 keV, in this work was investigated the attenuation properties of P(VDF-TrFE)/Bi_2O_3 and P(VDF-TrFE)/ZrO_2:8%Y_2O_3 composites just for XRQ5 (70kV) beam quality. Investigation concerning the other beam qualities is in progress. The radiochromic film calibration was

done by irradiating samples with doses ranging from 20 to 100 mGy, for the beam quality RQR5 (70kV). In Figure 4, the films become darker when the dose is increased.

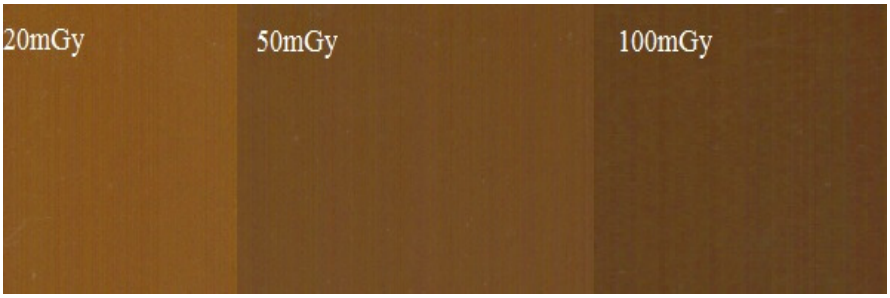


Figure 4: XR-QA2 Gafchromic® radiochromic films scanned at high resolution mode. The films were irradiated with 20, 50 and 100 mGy, provoking a gradual darkening for increasing doses.

The color intensities seen in Figure 4 were depicted into RGB components and the net red color intensities plotted against doses, as shown in Figure 5. After scanning at high resolution mode, the net red color intensity component has been observed to increase for increasing doses. The experimental data were fitted with an exponential curve, than can be expressed as

$$I = a \,.\, e^{-(D/b)} + c \qquad (1)$$

where I is the net red intensity, D is the delivered dose and a, b and c are contants. For this fitting $a = -78.56$, $b = 30.68$ and $c = 79.16$. The correlation factor *R-square* was 0.988.

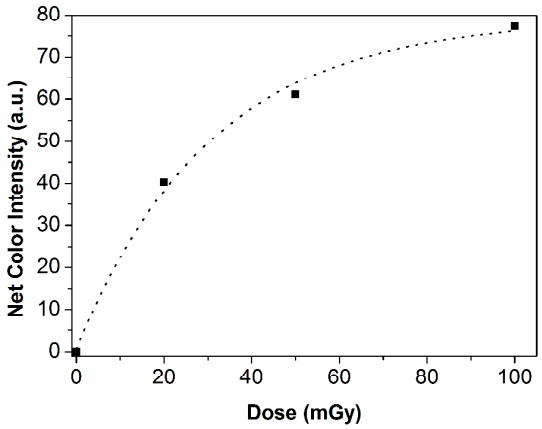


Figure 5: Exponential fitting for the red optical densities in radiochromic films as a function of delivered dose

After the calibration process, the composites samples were sandwiched between two sheets of XR-QA2 films in order to evaluate their capacity of shielding the XRQ5 beam quality radiation. In order to attenuation investigate was made scanner of the XR-QA2 films directly exposed to the X ray beam and under composite sample. These images scanned were analyzed by tools of the Image J® software.

Figure 6 show the P(VDF-TrFE)/Bi_2O_3/MAA composites samples, with different concentrations %Bi_2O_3. In this Figure the net red color intensities are plotted to the Bi_2O_3/MAA concentration in the composite (left axis). The radiation attenuation factor, calculated as the ratio between the dose measured by the frontal XR-QA2 film and in the one under the P(VDF-TrFE)/Bi_2O_3/MAA composite, is also plotted against the Bi_2O_3 concentration (right axis). The radiation attenuation factor, calculated as the ratio between the dose measured by the frontal XR-QA2 film and in the one under the P(VDF-TrFE)/Bi_2O_3/MAA composite, is also plotted against the Bi_2O_3/MAA concentration (right axis). It was not observed significant variation in attenuation with increasing concentration. Further research is needed for this composite, once the metal is already well known in the literature for use as a radiation attenuating material.

The P(VDF-TrFE)/ZrO_2:8%Y_2O_3 composites samples, with 2.0, 4.0 and 8.0 at.% of ZrO_2:8%Y_2O_3 showed a significant reduction in the measured doses. The radiochromic films placed under the samples with concentrations of 2, 4 and 8 at.% of ZrO_2:8%Y_2O_3 showed different attenuations factors, as shown in Figure 7. In this Figure the net red color intensities are plotted against the ZrO_2:8%Y_2O_3 concentration in the composite (left axis). The radiation attenuation factor, calculated as the ratio between the dose measured by the frontal XR-QA2 film and in the one under the P(VDF-TrFE)/ZrO_2:8%Y_2O_3 composite, is also plotted against the ZrO_2 concentration (right axis). The sample with 8 at.% of ZrO_2 showed the best shielding factor, with a dose reduction factor equal to 17.1 %. The radiation doses were evaluated by XR-QA2 films. It is possible see that increasing ZrO_2 concentration the attenuation factor increases following an exponential behavior, at least for these three concentration levels studied here. It is also an interesting result, indicating that maybe there is an optimal concentration level, which may turn these composites economically viable in the future reducing the skin doses in most of the high dose procedures.

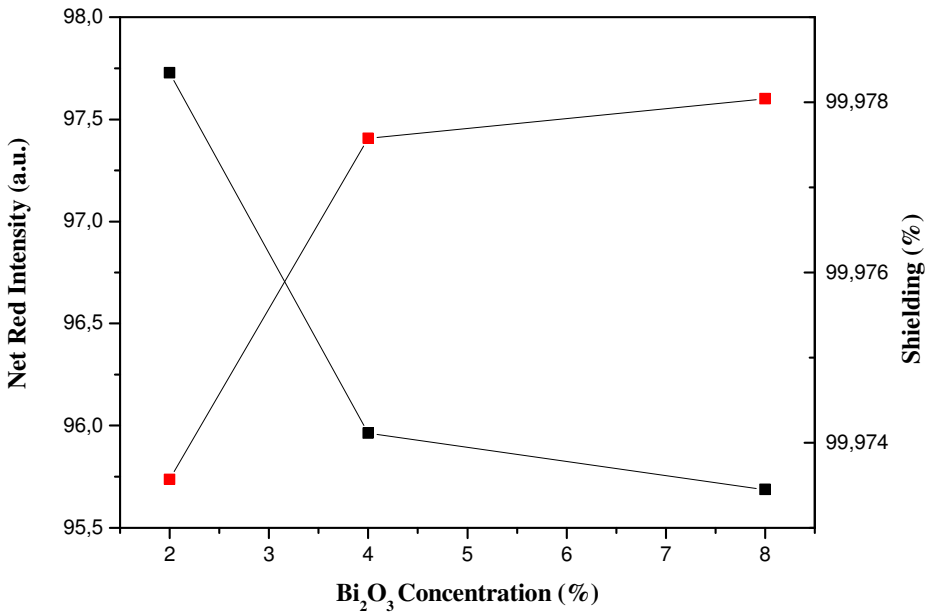


Figure 6: Plot of Bi_2O_3 /MAA concentrations in the P(VDF-TrFE):Bi_2O_3 /MAA composites as a function of the net red color intensity (left axix) and the radiation attenuation factor of RQR5 beam quality.

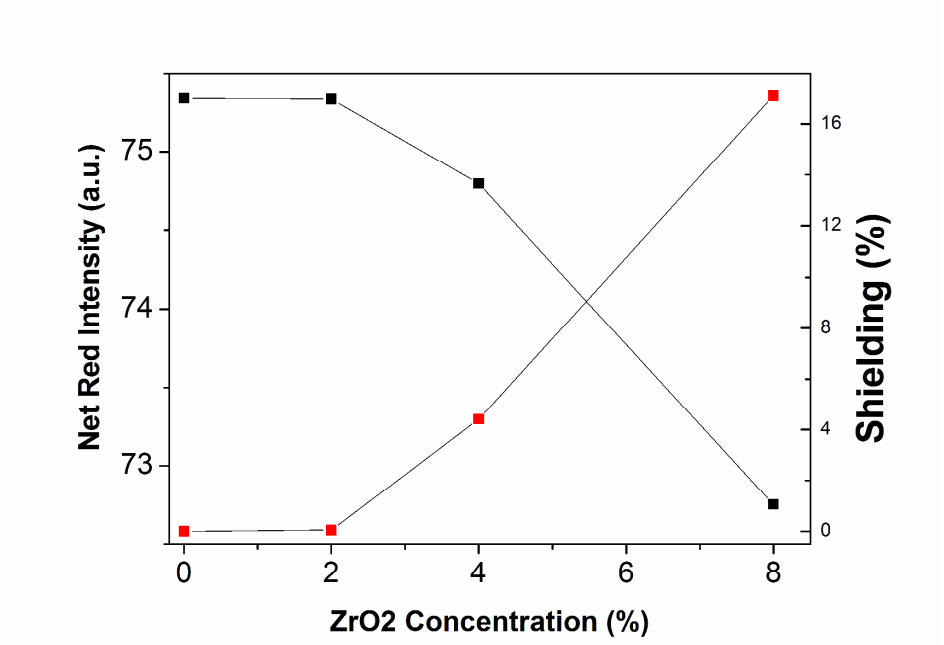


Figure 7: Plot of ZrO_2 concentrations in the P(VDF-TrFE)/ZrO_2:Y_2O_3 composites as a function of the net red color intensity (left axix) and the radiation attenuation factor of RQR5 beam quality.

4. CONCLUSIONS

P(VDF-TrFE):Bi_2O_3/MAA and P(VDF-TrFE)/ZrO_2:8%Y_2O_3 composites were produced by casting. In FTIR analyses can be observed 667cm^{-1} and 722cm^{-1} bands that are associated with the Yttrium presence in to P(VDF-TrFE)/ZrO_2:Y_2O_3 at 8% sample while 470 cm^{-1} band can be attributed to doubly degenerate bending vibrations of [BiO_6] units and 840-880 cm^{-1} band is showed to characteristic Bi-O stretching vibrations of BiO_3 units in to P(VDF-TrFE)/Bi_2O_3 sample.

The dosimetric characterization was performed by using XR-QA2 radiochromic films. P(VDF-TrFE)/Bi_2O_3 composites did not present significant variation in attenuation with increasing concentration. Further research is needed for this composite. The P(VDF-TrFE)/ZrO_2:Y_2O_3 films demonstrated follow an exponential increase for increasing ZrO_2:Y_2O_3 concentrations between 2 and 8 at.%. The attenuation factor for the P(VDF-TrFE)/ZrO_2 nanocomposites doped with 8 at.% of ZrO_2, irradiated with 100 mGy in RQR5 quality beam, is 17.1% which indicates that these nanocomposites have great potential to be use as protective attenuators in high dose radiology procedures. These results suggest that composites with filler by Bi_2O_3 and ZrO_2:Y_2O_3 materials can be applied as shielding of X ray radiation in high dose radiology procedures.

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