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Increasing X-ray to visible transduction performance of Gd_2O_3:Eu^{3+}PVDF composites by PPO/POPOP addition

J. Oliveira [a, b], P.M. Martins [a, b], P. Martins [a, b], V. Correia [a, b], J.G. Rocha [b], S. Lanceros-Mendez [a, c, *]

[a] Centro/Departamento de Física, Universidade do Minho, Braga, Portugal
[b] Centro Algoritmi, Universidade do Minho, Guimarães, Portugal
[c] BCMaterials, Parque Científico y Tecnológico de Bizkaia, 48160 Derio, Spain

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ABSTRACT

Polymer based scintillator composites have been produced by combining poly(vinylidene fluoride), PVDF, and Gd_2O_3:Eu^{3+} scintillator nanoparticles. Additionally, 2,5 dipheniloxazol (PPO) and (1,4-bis (2-(5-phenioxazolil))-benzol (POPOP) were introduced in the polymer matrix in order to improve visible light yield under x-ray irradiation. It is shown that addition of PPO and POPOP has no influence on the polymer structure, increases dielectric constant from ~7 to ~14, which is suitable for improving energy resolution, and increases in 40% the overall transduction performance of the composite without sacrificing its homogeneity and transparency. Thus, the developed Gd_2O_3:Eu^{3+}/PPO/POPOP/PVDF composites are appropriate for large area X-ray radiation detectors.

1. Introduction

Polymer nanocomposites represent one of the most important areas for the development of novel application oriented materials [1]. Such composites have been extensively studied for an increasing number of applications including catalysts, functional textiles, biomedical materials, sensors, actuators and materials for energy conversion and storage, among others [2,3]. It has been shown that, in such composites, both physical and chemical properties can be enhanced and/or tailored by the presence of suitable amounts of micro or nanofillers [4]. Thus, mechanical, electrical, optical and thermal properties have been improved with respect to the single polymer or co-polymer matrix [1].

Nanocomposites can be used to develop polymer based materials able to convert X-ray radiation into visible light, with appropriate mechanical properties, thermal, chemical and radiation stability, as well as with high energy resolution [5]. The conversion of X-ray radiation into visible light is based in the scintillation process: the interaction of the X-rays with electrons within the scintillator nanoparticles leads to their promotion to the conduction band across the band gap. Then, the electrons migrate to the activation center excited-state orbitals and the holes in the valence band to the activation center ground-state orbitals [6]. Finally, the transition of electrons from an activated center excited-state orbital to an activation center ground-state orbital produces a scintillation photon. Polymer based scintillators offer unique important properties such as mechanical flexibility and relatively high scintillation efficiency [1]. Additionally, such polymeric scintillators allow suitable response time, air-stability, low cost, easy fabrication in large areas in a wide range of geometries and tailored property possibilities through composition modification [7,8]. Polymer composites have been used, such as polystyrene with 2,5 diphenyloxazole (PPO) and 1,4 di[2-(5phenyloxazolyl)]benzene (POPOP), for the development of X-ray detectors for several applications [9]. Among the best ones, Gd_2O_3:Eu^{3+}/poly(vinylidene fluoride) (PVDF) composites were found to be able to convert X-ray radiation into visible light [4]. In this system, PVDF was used as a binder since it is a flexible and stable matrix and due to its low surface tension and high thermal and light degradation resistance [4,10]. Gd_2O_3:Eu^{3+} nanoparticles were selected as scintillators due to their wide band gap (~5.2 eV), atomic number, high density (~7.4 $g \cdot cm^{-3}$), suitable light yield (~2×10^4 photons$\cdot$$MeV^{-1}$) and radioluminescence.

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* Corresponding author. Centro/Departamento de Física, Universidade do Minho, Braga, Portugal.
E-mail address: lanceros@fisica.uminho.pt (S. Lanceros-Mendez).

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Nevertheless, in order to meet industry requirements, the light yield in such innovative polymer composites needs to be improved, without sacrificing the homogeneity and transparency of the scintillators [11–14]. Such improvement will allow X-ray dose reduction, decreasing signal to noise ratio, increasing sensitivity and optimizing the detection efficiency [11,12].

In this way, aiming to fulfill the present needs in the field of X-ray detection, this work focuses on the improvement of the light yield in the overall X-ray to electrical conversion process by the inclusion of fluorescence PPO and POPOP within the scintillator composites. Such light yield improvement allied with the good mechanical properties, thermal, chemical and radiation stability, large areas potentiality, homogeneity and transparency found on the Gd_2O_3:Eu^{3+}/PVDF composites will allow the use of Gd_2O_3:Eu^{3+}/PPO/POPOP/PVDF scintillator composites for the development of novel x-ray detectors [5,11,15,16].

2. Experimental

Composite films of Gd_2O_3:Eu^{3+}/PVDF, with and without PPO/POPOP, with a thickness of ~50 μm were prepared by solvent casting and melt processing. First, based on [1], the desired content of Gd_2O_3:Eu^{3+} (0.25 and 0.5 wt.%) nanoparticles was added to dymethylformamide (DMF) and placed in an ultrasound bath. Then, PVDF was added to the mixture and placed in a Teflon™ mechanical stirrer until complete dissolution of the polymer. After adding the fluorescence material to the solution, 1 wt.% of PPO and 0.01 wt.% of POPOP, it was spread in a clean glass substrate and placed in an oven at 250 °C for 10 min before cooling down to room temperature. Such fluorescence content has been previously optimized in order to maximize light yield [17–19]. Additionally, the selected weight ratio allows to achieve high phenyl concentration in the matrix, hereby increasing the number of excimer states which transfer the network excitation energy and avoiding optical inhomogeneity and opacity [14].

The phase of PVDF was determined from the Fourier transformed infrared (FTIR) spectra collected in a Perkin–Elmer Spectrum 100 from 650 to 4000 cm^{-1}.

The optical transmittance of the samples was obtained by a double beam spectrophotometer UV-2501PC Ultraviolet–Visible (UV–VIS) set up in the 200–800 nm range with a 1 nm step.

ε' and ε'', real and imaginary parts of the dielectric function, were obtained [20,21] through the measurement of the capacity and tan δ (dielectric loss) with an automatic Quadtech 1929 Precision LCR meter. The samples were previously coated with circular Au electrodes with 5 mm diameter onto both sides of the sample in order to obtain a parallel capacitor geometry.

Characteristic I–V curves were measured at room temperature with a Keithley 6487 picoammeter/voltage source in a voltage range from −75 to 75 V. The DC conductivity was obtained from the slope of the I–V curves and the geometrical characteristics of the samples. The efficiency of the X-ray radiation into visible light conversion was measured with the help of a Bruker D8 Discover diffractometer using Cu Kα incident radiation at 40 kV applied voltage and current varying from 10 to 40 mA. The output visible light from the samples at the corresponding wavelength was detected by a TSL2560 photodiode from Texas Ad. Optoelectronic Solutions Inc.

3. Results and discussion

Fig. 1a shows the FTIR spectra of neat PVDF and Gd_2O_3:Eu^{3+}/PVDF composites, with and without PPO/POPOP, in order to evaluate the influence of the filler on the polymer phase. Further, the optical transmittance as a function of wavelength for the pristine polymer and composite films is shown in Fig. 1b. The following nomenclature will be adopted in the text: PVDF/0.25S-FL means a PVDF sample with 0.25% of scintillating fillers in the present of fluorescent (FL) material.

The introduction of Gd_2O_3:Eu^{3+} nanoparticles and fluorescence molecules into the PVDF matrix has no influence in the polymer phase content. The polymer crystallized in the α-phase, as demonstrated by the presence of the 766, 795 and 976 cm^{-1} characteristic bands and absence of the bands related to the polar β and γ phases [1,22]. This fact is related with the sample preparation conditions [1], melting and recrystallizations, but also indicates that there is no nucleation of the polar phases due to strong electrostatic surface interaction between fillers and the monomer dipolar moments, as it has been previously observed in other nanocomposite systems [23–25].

Fig. 1b shows just a small decrease of ~8% in the optical transmittance of the samples with the introduction of the fluorescence molecules when compared to α-PVDF and to the composite without fluorescence molecules. This fact is related to the filler content of the samples, leading to a more heterogeneous and defective microstructures, which causes dispersion of the light and leads to lower visible light transmittance [22].

Since the energy resolution of the systems can be improved by increasing the dielectric permittivity of the scintillator material [26,27], dielectric properties of the composites have been determined (Fig. 2).

Fig. 2a shows that the dielectric response of PVDF slightly increases with the incorporation of Gd_2O_3:Eu^{3+} nanoparticles, from $\varepsilon' = 6$ to $\varepsilon' = 7$, and shows a significant increase, from $\varepsilon' = 6$ to $\varepsilon' = 14$, with the incorporation of the fluorescent molecules (Fig. 2b). The first effect is related with the filler/polymer interfacial effects and increased ionic conductivity of the PVDF matrix with the introduction of Gd_2O_3:Eu^{3+} nanoparticles [1], whereas the high dipolar moments of the fluorescence molecules explain the second one [28]. This increase, does not occur in tan δ, which remains practically constant, at a given frequency, independently of the nanoparticle concentration and the introduction of the fluorescence molecules (Fig. 2b).

In order to evaluate the performance of the developed composites for X-ray detector applications, X-Ray radiation was projected into the composite films and the conversion into visible light was measured by a photodetector (Fig. 3).

The samples were placed on the sample holder, that included the block acquisition system (B.A.S.) constituted by the electronic read-out circuit, a battery, a TSL235 light sensor and a Micro Control Unit (MCU) CC1111 [29] both from Texas Instruments (Fig. 3).

Fig. 4a shows the variation of the visible radiation intensity (V.R.I.) as a function of X-ray intensity. The variation of the visible radiation intensity as a function of Gd_2O_3:Eu^{3+} content is shown in Fig. 4b.

Results show that visible light yield increases with increasing Gd_2O_3:Eu^{3+} filler content as well as with the introduction of fluorescence materials up to 0.50 wt.% (see Fig. 4b).

Due to the interaction with the X-rays, electrons within the Gd_2O_3:Eu^{3+} nanoparticles are promoted across the band gap to the conduction band. Then, electrons migrate to the activation center excited-state orbitals and the holes in the valence band to the activation center ground-state orbitals, giving rise to the scintillation light [1,30,31]. The overall visible light yield strongly increases with the addition of fluorescence molecules. In particular, it is observed that the overall increase in the efficiency of the X-ray to visible light yield is around 40% when fluorescence molecules are added to the composite. In this composites, the primary fluorescent molecule (PPO) absorbs the scintillation light matched to excited states in the base material and the second fluorescent