Pellets of Oyster Shell for High Dose Dosimetry: Preliminary Study

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Abstract
Several kinds of silicates have demonstrated their usefulness as radiation detectors for high dose dosimetry. In this work, oyster shell powdered samples were tested for high doses using the thermoluminescence (TL) and thermally stimulated exoelectron emission (TSEE) techniques. Pellets were obtained from the oyster shell powder mixed with Teflon followed by a sinterization process of thermal treatments of 300°C/30min and 400°C/1.5h. The TL glow curves showed two peaks at 110 and 220°C, and in the TSEE case, two peaks at 120 and 180°C. The main dosimetric properties were studied: reproducibility, dose-response curves and lower detection limits. The preliminary results showed the potential use of the studied material as radiation detectors.

Introduction
The mean objective of the study of new materials is to identify and to overcome the limits imposed, naturally, for their physics and chemical properties (McLaughin *et al*, 1989). The research of new materials applied in dosimetry and other activities that involve ionizing radiations began as early as 1663 when Robert Boyler reported his observations to the Royal Society in London (Becker, 1973). Thereafter several researchers have published results about new materials. In the radiation metrology research group at IPEN some works have been carried out with silicates. Caldas (1989), Caldas and Souza (1991), Teixeira (2004) studied the dosimetric properties of Brazilian and imported glasses applied to gamma and electron radiations. The dosimetric properties of jade and inossilicates were carried out by Melo et al (2004; 2008). They studied the dose-response in the range of 10Gy to 20kGy through the thermoluminescent (TL) technique, verifying the linear behaviour between 10Gy and 1kGy, and the sublinear behaviour between 100Gy and 20kGy, using the thermally stimulated exoelectron emission technique.

Other materials as the calcium-based phosphors have been studied and showed good dosimetric properties. Since the 60's these materials have been studied by several researchers. Among them are Medlin (1968) and Nambi and Mitra (1979), that used the TL technique, to study these materials; they verified that calcites are strong emitters of

TL; the dose response is linear up to 2 kGy. Bapat and Nambi (1975) showed that the calcite response becomes sublinear at higher doses before reaching a maximum intensity at a dose of about 20kGy, and the TL emission spectra consist of a broad band with maximum at 630µm.

The components that form the oyster shell are $CaCO_3$, CaO, SiO_2, MgO, Al_2O_3, SrO, P_2O_5, Na_2O and SO_3 (Yoon *et al*, 2003, Freire *et al*, 2009). In addition to all these compounds, there are trace amounts of Mn^{2+}, Pb^{2+}, Ce^{3-}, $(UO_2)^{2+}$, Dy^{3+}, Sm^{3+}, Tb^{3+}, Nd^{+3}, Eu^{3+} that are responsible for the luminescence of calcite and for a radiation-induced center of violet emission (Marfunin, 1979). Although the oyster shell is formed by many compounds, the $CaCO_3$ (calcium carbonate) corresponds to approximately 96% of material that forms it. Calcium carbonate is found in two polymorphic forms, calcite (rhombohedral) and aragonite (orthorhombic) (Ikeya, 1993). The aragonite is only meta-stable under ambient conditions, transforming to calcite on heating. A reconstructive aragonite to calcite transformation takes place in the 300 – 400°C range in biogenic samples (Balmain e*t al*, 1999). Due thermal treatment the luminescence in $CaCO_3$, that is due to band-to-band recombination, will blueshift or enhance the higher energy part of the spectra (Medeiros *et al*, 2006).

TL signal is present in two polymorphic forms and caused by presence of Mn^{2+}. This presence of Mn^{++} results in glow peaks at 180° and 250°C in aragonite (Medlin, 1963), strong glow peaks at 80° - 100°C and weaker ones at 150°-175°, 215°-230°C and 320° - 330°C in calcite (Sunta,1985).

The objective of the present work was to study of the dosimetric properties of gamma induced centers in marine oyster shell using the TL and TSEE techniques.

Materials and methods

The materials studied in this work, known as oyster shells (Figure 1), usually used for decoration, were obtained in a market of Recife city originating from the northwest coast of Brazil. The pellets were prepared mixing powered oyster shell, with diameter between 177µm and 74µm, with powered Teflon in a 1:2 proportion.

Fig. 1. a) Bracelet made of natural oyster shell; b) pellets of oyster shell powder with Teflon and c) powder of oyster shell on an aluminium foil.

The oyster shells were powered and sieved retaining the 177µm – 74µm size fraction. The samples were thermally treated at 300ºC/1h and kept in dark until the irradiation and the TL and TSEE measurements were performed. After the treatments the pellets were irradiated at room temperature using a ^{60}Co panoramic source of the Centre for Radiation Technology (IPEN), and a ^{60}Co radiotherapy source of the Centre for Radiation Metrology. The pellets were irradiated with doses in the range from 5Gy to 10kGy. All measurements were taken at room temperature, and the pellets were sandwiched in Lucite plates with 3.5mm thickness to guarantee the electronic equilibrium during the irradiations. The TL measurements were taken using a Harshaw TL reader model 2000 A/B in the range from 50° to 300°C and the TSEE measurements were taken using a home-made system developed at the Centre for Radiation Metrology in the range from 30° to 300°C. All TL and TSEE measurements were obtained with linear heating rates of 10ºC/s in nitrogen flux and P10 flux, respectively.

Results

The TSEE measurements show peaks appearing at approximately 120°C and 180°C (Figure 1a). The TL emission curve, presented in Figure 1b, shows two characteristic peaks at 110°C and 220°C.

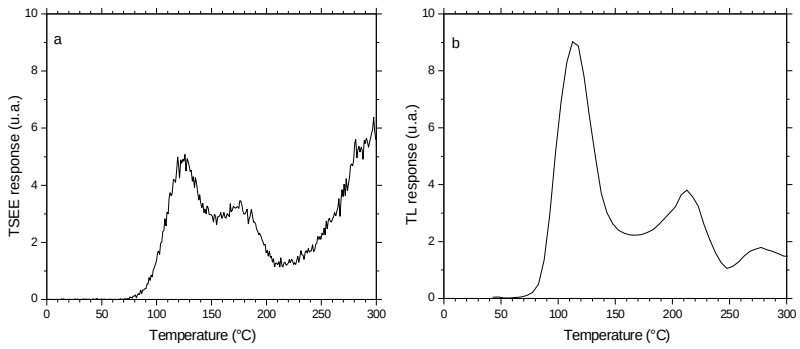

Fig. 1. TSEE(a) and TL(b) curves of the oyster shell in pellets, irradiated to 400Gy at room temperature, using a ^{60}Co source.

Figure 2 shows the dose-response curves of oyster shell pellets irradiated (^{60}Co) at room temperature over a range of 5Gy to 10kGy. The curve shows the increasing behaviour in function of the absorbed dose. The maximum standard deviation for the dose response curves was 3.5% for TSEE measurements (Figure 2a) and 4.5% of the TL measurements (Figure 2b).

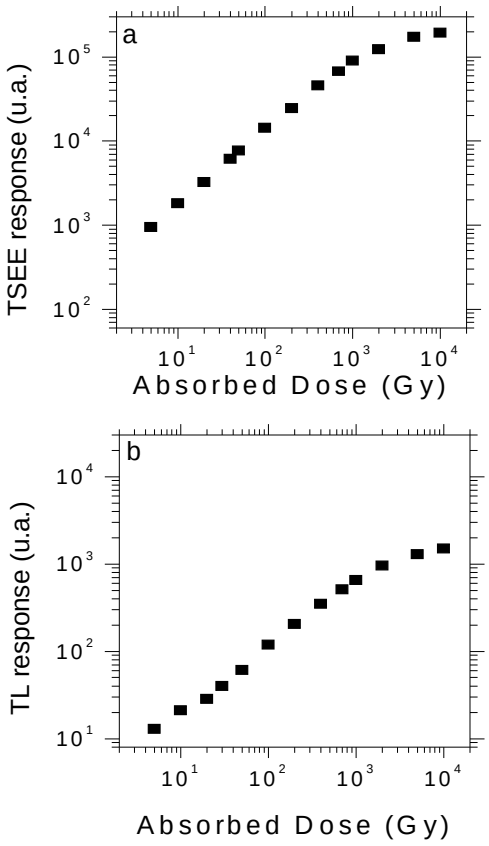

Fig. 2. TSEE (a) and TL (b) dose-response curves of the oyster shell in pellets, irradiated at room temperature, using a ^{60}Co source.

Reproducibility tests were carried out in samples irradiated to 5Gy (^{60}Co) at room temperature. The thermal treatment used before each irradiation of the samples was 300°C/1h. The maximum standard deviation, for irradiated samples, was 4.2% for TL measurements and 2.4% for TSEE measurements.

The lower detection limits were determined by variability studies of the TL and TSEE responses of samples treated at 300°C/1h and not irradiated. The value obtained using the detection of triple standard deviation of the samples was 500mGy.

Discussion

The results obtained show that oyster shells present possibility of use in high dose dosimetry. Oyster shells are biogenic materials in which the main minerals constituent is calcium carbonate. Observations carried out by Carmichael *et al* (1994) on the morphology of the oyster shells conclude that there is a great variation in the extent and type of mineralization. However, in studies carried out by Parker and Balmain *et al* (1999), they showed that a reconstructive aragonite to calcite transformation takes place in the 300 – 400°C. In the present work the pellets were made of powered oyster shell mixed with polytetrafluoroethylene and treated 400°C/1.5h, a procedure that probably transforms the aragonite in calcite.

The TL curves of calcium-based phosphors show two characteristic peaks at 175°C and 240°C (Anderle *et al*, 1998; Medlin, 1963; Nambi and Mitra, 1978) using a heating rate of 4.75°C/s. In the present work, the heating rate was 10°C/s that may have caused the dislocations of the TL peaks to 110°C and 220°C. The TSEE emission curve showed two peaks at 120°C and 180°C

The response of TL measurements shows a behaviour that agrees with that published by Bapat and Nambi (1975).

Conclusions

The good preliminary results of the studies with oyster shell samples in this work show the possibility of their use for high-dose dosimetry.

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