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Influence of Teflon® agglutinator on TLD spodumene pellets

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ABSTRACT

The possibility of using different materials for thermoluminescent dosimetry agglutinating their powder with Teflon® (a polymer) has been studied in recent years. In this paper the thermoluminescent properties of spodumene-Teflon® composites were studied exposing them to different doses of a ^{60}Co radiation source, in comparison to the thermoluminescent properties of crystalline powder and of Teflon. The thermoluminescent emission curve of pure Teflon® pellets showed two peaks at 200 and 250 °C at doses above 1 kGy, which may influence the dosimetry of high-doses that uses crystals agglutinated with this polymer. Preliminary results show that the Teflon® causes an increased sensitivity in the TL signal of the pellet compared to the crystalline powder without the polymer, and that even the pure Teflon® pellet is a material that can be exploited for high-doses dosimetry.

1. Introduction

The safe application of ionizing radiation in various areas requires the use of radiation detectors, i.e., equipment capable of detecting its presence or quantifying it. The study of these detectors, intimately linked to the understanding of the interactions that occur in the material, was also performed in this work.

In this context, a great emphasis has been given to thermoluminescence (TL), which is the light emitted by certain crystals, when heated, previously exposed to ionizing radiation. This emphasis is of great importance, since solid state dosimeters have been produced on a large scale for the measurement of radiation doses.

When applying for cohesive thermoluminescent dosimeters (TLD), common in many works is the use of the mixture of polycrystals and a polymer, with a ratio of 1 (polycrystalline):1 PTFE (polytetrafluoroethylene, a type of polymer) [1–3] or the proportion of 1 (polycrystalline):2 PTFE [4,5]. Each type of polymer is suitable for one or more applications, depending on their physical, mechanical, electrical, optical, and structure etc. The most used polymer type in the Brazilian market is the Teflon® (DuPont) that is a polymer, which has a chemical formula with branched carbon and fluorine. Quite inert and stable, it does not corrode, presents a very low attrition rate, does not react with other chemicals, and is widely used as a binder in the production of dosimeters (TLD) of $CaSO_4$.

After its molding, the crystallinity of the polymer can still be modified by heat. During heating, the polymer chains can move more freely, forming additional crystalline structures (crystallites). Therefore, in general, the polymers are neither fully amorphous nor fully crystalline [6].

The methodology for obtaining pellets synthesized using Teflon® as agglutinator eliminated problems of fragility and hygroscopicity of the detector and allowed to obtain thinner $CaSO_4$ detectors [7]. However, no studies on the effects of ionizing radiation on pure Teflon® have been conducted yet.

In this work, the influence of Teflon® was verified in a different type of TLD. The natural lilac crystal of α-spodumene, a lithium aluminum silicate ($LiAlSi_2O_6$), was chosen because it presents a rather interesting luminescence. This lithium pyroxene is relatively abundant in nature, and it presents both thermoluminescent and radioluminescent quite intense properties. Moreover, their thermoluminescent peaks appear in temperatures and wavelengths suitable for TL dosimetry or even dating [8–12]. The objective was also to investigate the possibility of using Teflon®-spodumene composites for dosimetry. The preliminary structural and dosimetric characteristics of samples of Teflon® and α-spodumene-Teflon® pellets were analyzed.

2. Experimental

All pellets were produced in the Laboratory for Dosimetric Materials Production of the Instituto de Pesquisas Energéticas e Nucleares (IPEN).

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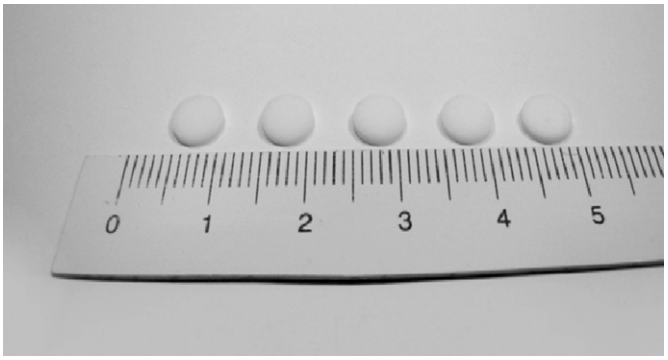

Fig. 1. Teflon® pellets.

A set of 35 pellets was produced with Teflon®/PVA (polyvinylacetate [–H_2CH (O_2CCH_3)-n], Teflon® as agglutinator), with a final mass of 50.0 mg, diameter of 6.0 mm and 2.0 mm in thickness (Fig. 1). For their sintering, they were exposed to thermal treatments of 300 °C for 30 min and 400 °C for 1.5 h in a microwave oven, CEM Corporation, USA. It is known that the temperature of Teflon® fusion is around 330 °C. [13].

Samples of Teflon® powder used in the preparation of the pellets were analyzed by X-ray fluorescence (XRF) with a Rigaku spectrometer, model ZSX Mini II, operating with a tube of Pd (power 40 kV × 1.2 mA) from the Physics Department, Federal University of Ceará (UFC).

The pellets were exposed to gamma radiation, using the Gamma-Cell System of ^{60}Co (dose rate of 1.96 kGy/h), of the Center for Radiation Technology/IPEN, with doses ranging from 50 Gy to 30 kGy. The irradiations were performed at room temperature (RT), and the samples were fixed between 3.5 mm thick Lucite plates to ensure electronic equilibrium conditions during irradiation.

20 pellets were also produced sintering natural α-spodumene agglutinated with Teflon® (Dupont) powder. The samples of natural α-spodumene used in this work are from the region of Governador Valadares (MG) Brazil, and they present a lilac color in the *c*-axis direction or pale yellow color in the other observed directions. The spodumene is called kunzite (lilac spodumene) whenever the Mn/Fe concentration rate is larger than 1 [14]. This ratio in the sample here investigated is equal to 1.11; it is part of a previously studied sample [12].

The crystals of α-spodumene were crushed in a mortar with the aid of a pestle, both of agate, and were sieved to select grains between 0.180 mm and 0.075 mm. The grains were selected and mixed by hand with Teflon® powder in a ratio of 1:2, α-spodumene and Teflon®, respectively. The mixture was placed in an alumina crucible, taking care of optimizing the stirring until homogenization. Then the mixture was pressed at 1.6×10^{11} N/m^2 to obtain 20 mg pellets, with 2.0 mm in thickness and 6.0 mm in diameter. They were then sintered, at 300 °C/30 min and 400 °C/1.5 h in a microwave oven, CEM Corporation, USA. The sample cooling was carried out slowly in the oven. Afterwards, X-ray Diffraction (XRD) measurements were taken with a powder diffractometer Rigaku RINT 2000/PC, with CuKα radiation ($\lambda = 1.5418$ Å), with the tube operating at 40 kV/25 mA in the continuous mode with steps of 2° min^{-1}.

The powder samples of spodumene and the spodumene-Teflon® pellets were exposed at room temperature to gamma radiation, using a Panoramic System (^{60}Co, dose rate of 0.3583 kGy/h in Nov/2009), of the Center for Radiation Technology of IPEN, with doses from 10 to 50 Gy.

To evaluate the TL response of the powder and pellets, a Harshaw TL reader system, model TLD-3500, was utilized; after the TL measurements, the samples were thermally treated at 300 °C/1 h for their reuse.

3. Results and discussion

The chemical composition of the Teflon® sample analyzed by XRF is shown in Fig. 2. This method does not detect light chemical elements due to low energy photons. The detection difficulty of lighter elements gradually increases as the atomic number becomes lower than 23. In this case, the elements carbon and fluorine found in Teflon® were not detected. Since the impurities detected (Ca, Al, and K) at low concentrations are easily found in nature, it is likely that during the preparation the sample may have been contaminated by them, despite all care in its handling.

The diffraction pattern of Teflon® can be seen in Fig. 3(a). This same type of material can be found in the literature used in the production of thin films [15]. It is possible to confirm that this type of Teflon® nor has a fully amorphous and neither a crystal structure [6]. Different brands of Teflon® may present different crystal structures and different chemical compositions. Therefore, extreme care must be taken in the production of pellets using Teflon® as agglutinator, because the repeatability of the luminescent signal emitted by them can be influenced by these changes.

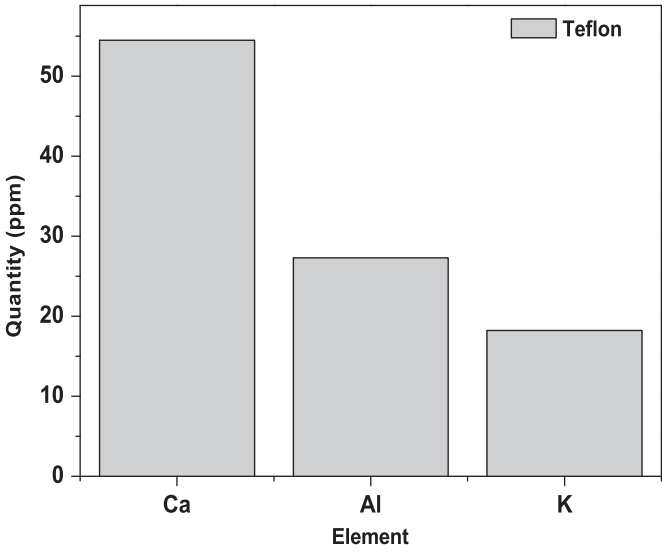

Fig. 2. Ion concentration of impurities found in a Teflon® sample using the X-ray fluorescence technique.

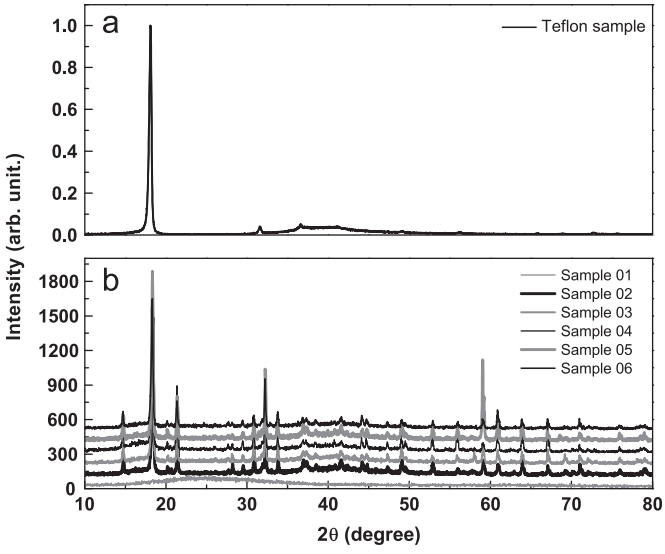

Fig. 3. X-ray diffraction pattern of (a) Teflon® powder and (b) 6 pellets of spodumene-Teflon®.

To check the repeatability of the crystal structure in the composites agglutinated with the same type of Teflon® that have undergone the same preparation procedures, XRD measurements of 6 pellets of spodumene-Teflon® produced similarly were taken. In this analysis, Fig. 3(b), almost all samples showed the same pattern of X-ray diffraction, i.e. they have the same crystalline structure. However, one of the pellets (sample 1) presents a completely different pattern, which is expected from an amorphous structure without XRD peaks. One possible explanation for this variation is that there has been an increase in the amount of Teflon® in relation to the crystals of α-spodumene in this pellet. But even if the pellet was composed only of the agglutinator, the XRD peak characteristic of the polymer, shown in Fig. 3(a) should be seen.

Results in the literature of Differential Scanning Calorimetry (DSC) reported that during the heating of the polymer Teflon® phase transitions may occur. These changes occur during heating at 25 °C (transition triclinic to hexagonal) and at 33 °C (transition hexagonal/pseudo-hexagonal) [13]. In the same work it is shown that the melting point of the PTFE is about 336 °C. Thus it is possible that a phase transition of Teflon® may have occurred during the sintering of the sample, altering its crystal structure. This fact has to be investigated in future research, since the production of the TLDs should be repetitive, and such drastic changes should not occur in the pellets.

Fig. 4 shows the diffraction pattern obtained from the sample of natural α-spodumene powder and from a sintered pellet of spodumene-Teflon®. The identification of the crystal as the structure of α-spodumene was confirmed by comparing it with the diffraction pattern of α-spodumene ICSD 9668. It was also possible to identify the main and more intense peak of the agglutinated polymer, highlighted in Fig. 4.

The TL emission curves of powder and sintered pellets of α-spodumene are shown in Fig. 5. An increased sensitivity of the TL pellet in relation to the crystalline powder without Teflon® was observed. Moreover, the TL peaks are better defined in case of the pellets. One possible explanation may be that the contact with the heating material is better than when with only the mineral powder. Thus, the heating occurs more evenly and quickly over the entire content of the pellet, tapering the peak and making it more intense, a process that in the powder may be slower and less uniform. It should be also noted that one peak at about 320 °C is present only in the pellets but not in powder glow curves. This peak is probably due to the polymer.

The dose–response curves were obtained with samples of natural α-spodumene powder and α-spodumene-Teflon® pellets irradiated at doses of 10 Gy–50 Gy. Fig. 6 presents these results; in the case of the pellets a linearization of the curve occurs with respect to crystalline powder. These measurements showed a maximum relative standard deviation of 2.1%.

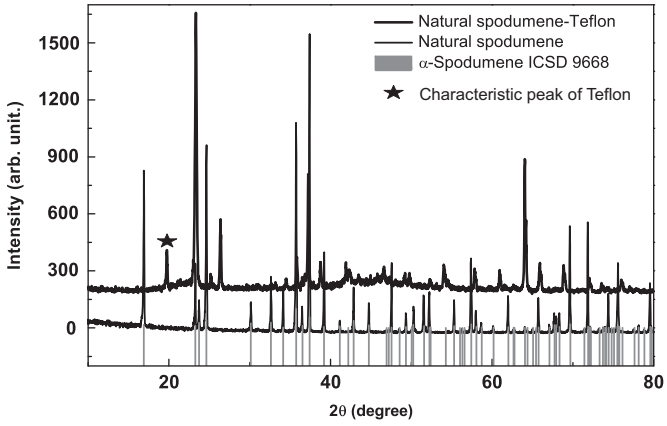

Fig. 4. X-ray diffraction pattern from a sample of natural α-spodumene powder and from a sintered pellet of spodumene-Teflon®.

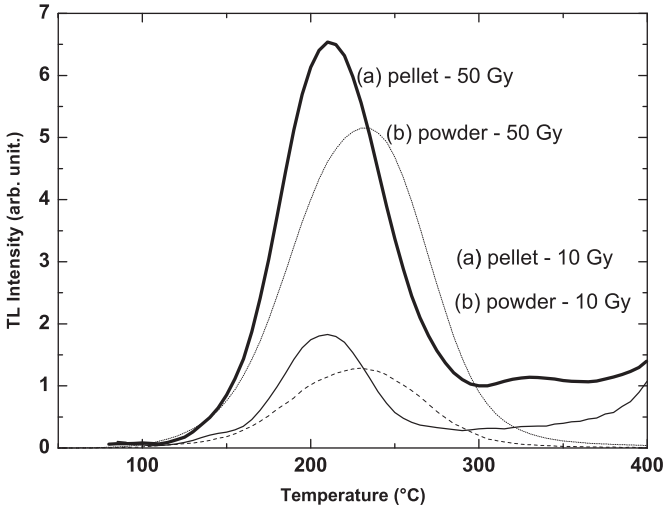

Fig. 5. TL emission curves of powder and pellets of α-spodumene-Teflon® irradiated with 10 Gy and 50 Gy (^{60}Co source) at room temperature.

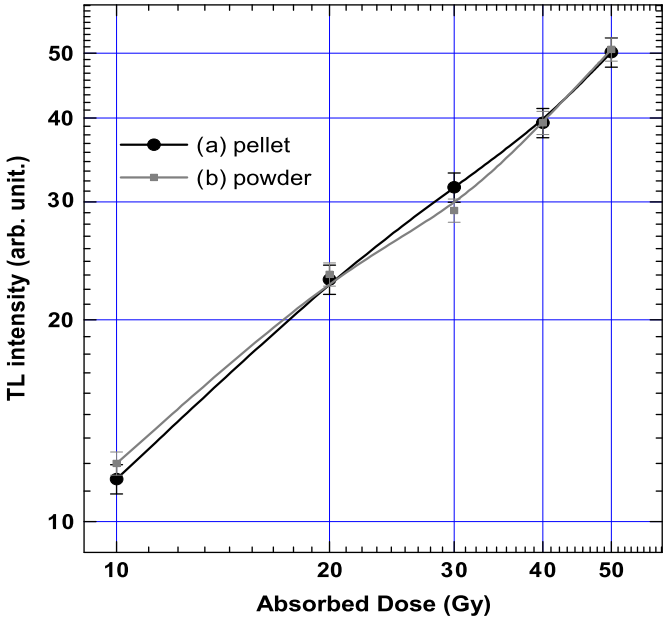

Fig. 6. TL dose–response curves for samples of (a) natural α-spodumene powder and (b) pellets of spodumene-Teflon®, both irradiated with doses of 10–50 Gy using a ^{60}Co source.

One objective was to investigate if the agglutinator alone emits TL light. Thus, only pellets made of Teflon®/PVA were irradiated with different doses of gamma radiation from 50 to 30 kGy. The emission curves obtained 1 h after irradiation are shown in Fig. 7. There are two intense TL peaks around 200 and 250 °C at about 1 kGy. As in the majority of the various TLDs for high doses, the main dosimetric peak appears in this temperature range; this fact may influence the signal emitted by the crystal that was agglutinated with Teflon®; this result is of great importance for a proper dosimetry. With 50 Gy it is possible to observe a shoulder at about 150 °C, which also can be seen in pellets in Fig. 5 irradiated with 10 Gy; however it is not presented in the powder glow curves, being attributed to Teflon®.

For high-dose dosimetry using TLDs agglutinated with Teflon®, it is recommended to heat the pellets at about 200 °C

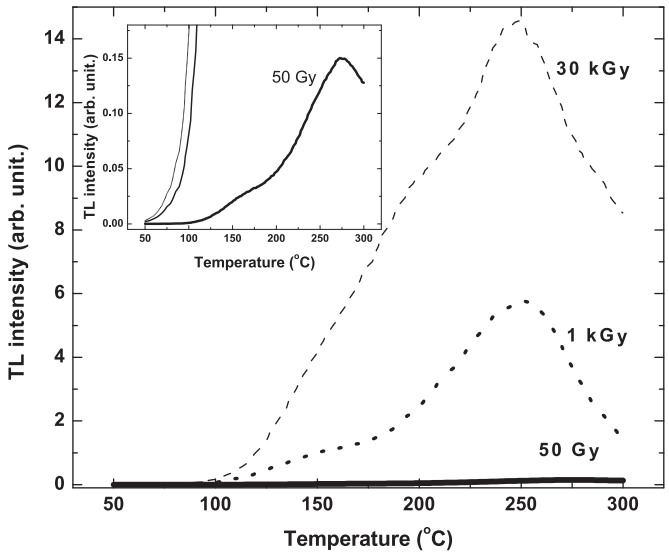

Fig. 7. Glow curves of Teflon® pellets irradiated with ^{60}Co. The inset shows the detail of glow curve of sample irradiated with 50 Gy.

after irradiation to eliminate the first TL peak of Teflon® and the shoulder at 150 °C if they affect the analysis, keeping only the signal of the second peak. Moreover, one can conclude that the pellet consisting only of Teflon® may be useful for dosimetry of high doses. A further study of this type of pellets is under development to verify their dosimetric characteristics.

4. Conclusions

This study shows that Teflon® does not only act as an agglutinator, giving greater strength to the pellets, but it may also contribute to the TL signal emitted by the TLD pellets agglutinated with this polymer for high doses of gamma radiation. In the case reported in this work using Teflon® as an agglutinator to spodumene crystals, a better definition of the thermoluminescent peaks, a higher linearity and an increased TL sensitivity of the pellets of spodumene-Teflon® (in relation to the crystalline powder without the polymer) were obtained. These results indicate that Teflon® may influence the shape and intensity of the TL signal. Therefore, to agglutinate crystalline powders, extreme care must be taken to avoid changes in the composition of the pellets, which could influence the final result of the produced thermoluminescent dosimeters.

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