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Physical, morphological and dosimetric characterization of the Teflon agglutinator to thermoluminescent dosimetry

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ABSTRACT

In preparing of thermoluminescent dosimeters (TLD) it is common to use as agglutinator the polytetrafluoroethylene (PTFE), called Teflon®. In this paper the physical, morphological and dosimetric characteristics of Teflon® were evaluated aiming its application in thermoluminescent dosimetry. The differential thermal analysis (DTA) and thermogravimetry (TG) results showed that the Teflon glass transition and melting points are of about 48 °C and 340 °C, respectively. By means of the X-ray diffraction technique, the crystallinity index K_c was estimated as 94%. Micrographs of Scanning Electron Microscopy (SEM) showed a cohesive surface in spodumene–Teflon pellets, as required for thermoluminescent dosimeters (TLD), leading to the conclusion that Teflon acts as binder, providing greater mechanical resistance to the TL pellets. However, Teflon may influence high doses dosimetry when it is applied as an agglutinator. Preliminary results of Teflon pellets dosimetric properties, with their dose–response curve between 50 Gy and 60 kGy, TL response reproducibility and minimum detectable dose, indicate the possibility of use of pure Teflon TLD in high-dose dosimetry.

1. Introduction

Polytetrafluoroethylene (PTFE), popularly known as Teflon since 1946 with the registered trademark of DuPont, is nowadays produced by different manufacturers. Although belonging to the group of thermoplastics, this material presents high melt viscosity relatively to other polymers [1]. This characteristic has been exploited for agglutination of luminescent powders in preparation of thermoluminescent dosimeters (TLDs) [2,3]. This methodology eliminated problems of fragility and hygroscopicity of the detector and allowed to obtain $CaSO_4$ detectors with smaller thickness [4,5]. Several samples of sand and minerals as topaz, amethyst, jasper and jade [6–11] were studied as high-dose TLDs using Teflon as agglutinator.

Each type of polymer is suitable for one or more applications, depending on their properties, as physical, mechanical, electrical and optical. Teflon is a branched polymer, and usually it is used in Brazilian market as a coating. After its molding, the crystallinity may be further modified by the thermal process. In this case, by heating, the polymeric chains can move more freely to form additional crystalline structures (crystallites). Therefore, in general, the polymers are neither totally amorphous nor totally crystalline [12].

Despite their common use in TLDs, the dosimetric, physical and morphological characteristics of Teflon, for example, during the sintering process and heat treatment of the TLD, are not reported in the literature. In the present work, the importance of this type of characterization is emphasized, verifying possible influences of Teflon on the dosimetric results. In this study, changes in physical or chemical properties of Teflon, depending on its heating temperature, and the estimative of the index of crystallinity, and some dosimetric properties of pure Teflon pellets were studied.

2. Experimental

Powder of Teflon® (polytetrafluoroethylene—PTFE) from DuPont, in virgin form, has been investigated by X-ray diffraction (XRD) to confirm its structure. The measurements were performed with a powder diffractometer Rigaku RINT 2000/PC, with CuKα radiation ($\lambda = 1.5418$ Å), with the tube operating at 40 kV/20 mA in the continuous mode with steps of $2^\circ\ min^{-1}$ at room temperature.

The differential thermal analysis (DTA) and thermogravimetry (TG) of Teflon powder were performed in order to evaluate changes in its physical or chemical properties as a function of temperature. A sample of 11.82 mg was heated with a heating

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rate of 10 °C/min in an SDT TA 2960 with a simultaneous system of TG/DTA and a platinum crucible in air atmosphere. TG curves were expressed as percentage of weight loss versus temperature in degree Celsius and DTA curves were expressed as the variation in temperature between the sample and reference versus temperature in degree Celsius.

Two types of pellets were produced with and without Teflon as polycrystalline binder.

Spodumene/Teflon® pellets were produced following the procedure described by d'Amorim et al. [13]. Spodumene crystals ($LiAlSi_2O_6$) were chosen in this study because of the interest in investigating their use as TLD for high doses [13]. The pellets were prepared with the objective of evaluating the porosity and microstructural morphology of the TLDs surface agglutinated with Teflon. The pellets of β-$LiAlSi_2O_6$/Teflon were observed in a scanning electron microscope Shimadzu SS-550 belonging to the Analytical Central, Department of Fundamental Chemistry, Federal University of Pernambuco, Brazil. Initially, vaporization of argon was performed to remove possible impurities from the pellet surface, which was then covered with a thin gold layer (approximately 20 mm) in order to provide electrical conductivity for a scanning electron microscopy (SEM) test. The micrographs were obtained at magnifications ranging from 35 to 4500 times in low vacuum.

Pure Teflon® pellets were produced by the Laboratory for Dosimetric Material Production of IPEN-SP following the reported procedure [10,11]. The pellets had a final mass of 50.0 mg, diameter of 6.0 mm and thickness of 2.0 mm . These 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 60 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. The TL response of Teflon was obtained with an Harshaw TL reader system, model TLD-3500; after the TL measurements, the samples were thermally treated at 300 °C/1 h for their reuse.

3. Results and discussion

Fig. 1 shows the diffraction pattern of Teflon® powder. There is an intense peak around 18° 2θ and three other peaks less intense in the range from 30° to 45° 2θ, superimposed on an amorphous halo (broad peak under the crystalline peaks) around 36° 2θ. The identification of the sample as Teflon® was confirmed with the combination of pattern PDF2 00-047-2217 from the program *X'Pert HigthScore Plus* version 2.2b (2.2.2), produced by PNAlytical, 2006. This same type of material is reported in the literature to be used for the production of thin films [14]. It is possible to confirm that this type of Teflon® nor has a fully amorphous and neither a crystalline structure [12] in the same material. 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.

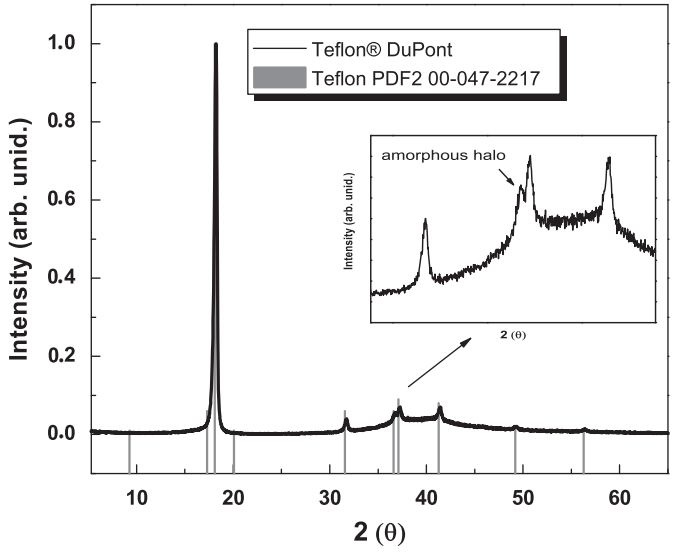

Fig. 1. X-ray diffraction pattern from a sample of Teflon powder (polytetrafluoroethylene) compared to pattern PDF2 00-047-2217.

The fraction of crystalline/amorphous reflects the level of crystallinity of the material, since the appearance of the crystalline regions can induce a "stretching" of the fibers in order to align the molecules and thus provides greater mechanical strength. According to Marinho [15], Teflon is a polymer that has higher crystallinity index (volume of the crystalline regions in the total polymer). In this work, the K_c crystallinity index of the studied sample was estimated as 94% by X-ray diffraction on the basis of peak areas corresponding crystalline (A_c) and area of amorphous halo (A_a) [16]:

$$K_c = \frac{A_c - A_a}{A_c} \times 100 \quad (1)$$

Samples of Teflon, in their virgin state or after polymerization, presented K_c between 85% and 95%, which can no longer be achieved after sintering [17]. It should be noted that this high degree of crystallinity is that which enables agglutination of various materials used for the thermoluminescent dosimetry. However, the final degree of crystallinity after partial melting and recrystallization depends on the cooling rate applied during the heat treatment, and ranges between 30% and 75% for the cooling rates normally used in industry [18].

TG and DTA tests were performed to estimate the initial temperature of the Teflon degradation and to establish the temperature limits in processes of sintering and heat treatment of the TLDs. TG is a technique in which the variation of mass of the sample is determined as a function of temperature and/or time. In the thermogravimetric analysis the sample weight is compared with an inert reference during a program of temperature variation at a constant rate. By DTA, the temperature of the sample is compared to an inert reference with a temperature program variation at a constant rate. Differences in temperature occur when the sample undergoes some endothermic or exothermic process. When a polymer is heated, the molecules vibrate with more energy and the transition from the glassy state to a malleable state may be possible. In this state, the polymer has higher volume, higher thermal expansion and higher elasticity [15]. The point at which this transition occurs is known as glass transition temperature (T_g). Other important points to certain polymers is the melting point (T_m) in which the molecules move independently of each other, and the thermal decomposition (T_d) at which occurs connections break, release of gases, color change and degradation.

The thermogram in Fig. 2 presents the T_g of PTFE at about 48 °C and the melting point at 340 °C, according to the endothermic peak. In its molten state, the polymer retains a large amount of energy which results in free motion of the chains. If a specific energy is added, it is possible to reach a point where the links begin to break up until a possible loss of properties, i.e. the thermal decomposition point (T_d). The thermal decomposition point of Teflon probably occurs from 400 °C.