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

R.A.P.O. d'Amorim [a], M.I. Teixeira [b], L.V.E. Caldas [b], S.O. Souza [a,*]

[a] Departamento de Física-CCET, Universidade Federal de Sergipe, 49100-000 São Cristóvão, SE, Brazil
[b] Instituto de Pesquisas Energéticas e Nucleares-IPEN-CNEN/SP, Av. Professor Lineu Prestes, 2242, 05508-000 São Paulo, Brazil

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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

* Corresponding author. Tel.: +55 79 32550729; fax: +55 79 2105 6807.
E-mail addresses: raquelalinepe@gmail.com (R.A.P.O. d'Amorim), miteixeira@ipen.br (M.I. Teixeira), lcaldas@ipen.br (L.V.E. Caldas), susanasouzalalic@gmail.com (S.O. Souza).

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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.

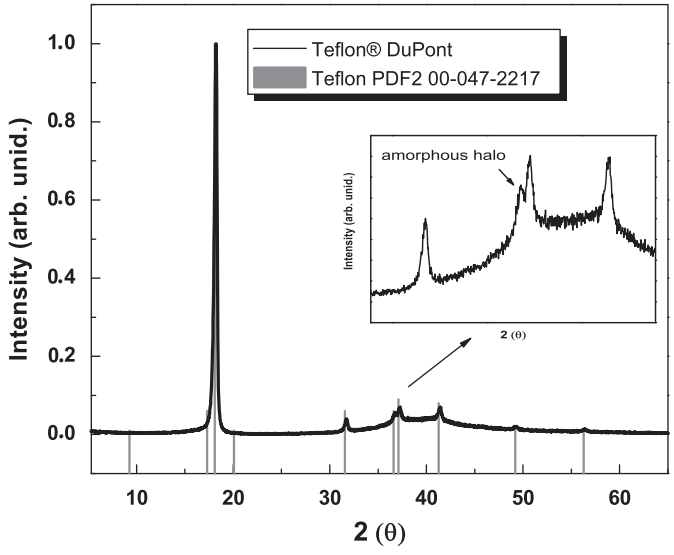

Fig. 1. X-ray diffraction pattern from a sample of Teflon powder (polytetrafluoroethylene) compared to pattern PDF2 00-047-2217.

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.

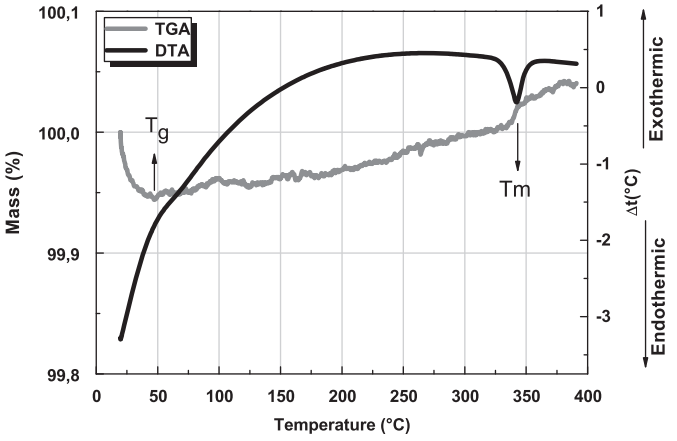

Fig. 2. DTA/TGA curves of Teflon® DuPont.

In general, the polymer powder sintering is carried out at atmospheric pressure and involves the application of controlled increase of heating temperature that exceeds the melting temperature and reaches a maximum (or sintering temperature) which is kept constant for a given time, called sintering time. Then, cooling is applied in controlled rate to room temperature [17]. In general, greater the structural rigidity of the polymer, higher is the melting temperature. The PTFE has four phases with different crystal structures that are dependent on the temperature and applied pressure. In this work, the sintering process of both types of pellets occurred at 300 °C for 30 min, followed by 400 °C for 1.5 h, according to the procedure reported in some previous studies [13,19]. As the melting point of Teflon was 340 °C, temperature of 400 °C for 1.5 h is suitable for sintering.

In the micrograph shown in Fig. 3(a) it can be observed that Teflon easily agglutinate the polycrystal, giving greater strength to TLD due to "stretch" of the fibers presented in detail in Fig. 3(b). This proves that Teflon easily adheres to the grains of spodumene, being capable to form a cohesive area as desired in the preparation of TLD dosimeters, since these types of dosimeters are reused several times, and durability of these is an essential factor.

Fig. 4(a) shows SEM image of produced spodumene/Teflon pellets. A cohesive surface can be seen as desired in the preparation of TLD dosimeters. However, in Fig. 4(b) it is shown that, despite having a cohesive surface, the inset has a damaged edge, presumably caused by manipulation with metal gripper. Thus, it is recommended that when using this type of gripper, a smooth and clean coating must be made in its tips. This coating can be made with polymers, as Teflon, or other soft material, easy to clean or replace. However, vacuum grippers are ideal for handling TLDs, because their use increase the dosimeter life.

Some dosimetric properties of pure Teflon pellets were studied, to verify the influence of this agglutinator in high-dose dosimetry. The TL glow curves of Teflon pellets irradiated with different doses are shown in Fig. 5. The measurements were performed 1 h after the irradiation. Two TL peaks can be observed, at 200 °C and 250 °C. Both TL peaks of these pellets are very intense for high doses and thus demonstrate that the use of Teflon as agglutinator may influence high-dose dosimetry.

The pellets irradiated with 30 kGy (^{60}Co) underwent thermal treatments at several temperatures for 15 min each with the objective to remove the TL peak at 200 °C. The most suitable thermal treatment to remove the first TL peak was 170 °C for 15 min, as can be seen in Fig. 6.

To determine the reproducibility of the TL response, five samples of Teflon pellets were studied, subjected five times to the same procedure: thermal treatment of 300 °C for 1 h (defined for its reuse), irradiation with ^{60}Co (2 kGy), thermal treatment of 170 °C for 15 min (to remove the first peak TL) and then TL measurement. The reproducibility of TL response obtained was 2.9%.

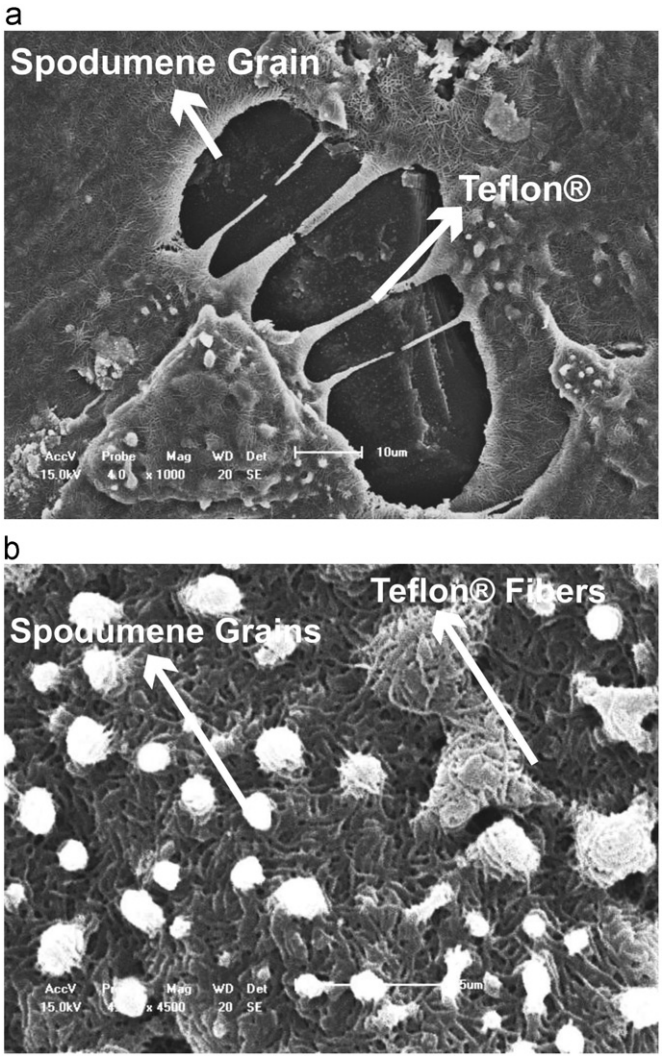

Fig. 3. Micrographs of pellets of spodumene/Teflon® (a) increase—1000 × and (b) increase—4500 ×).

Fig. 7 shows the dose–response curve, measured 1 h after each irradiation, obtained with pellets of pure Teflon irradiated with gamma doses from 50 Gy to 60 kGy after the thermal treatment of 170 °C for 15 min. These measurements presented a maximum relative standard deviation of 2.3%.

The minimum detectable dose of pure Teflon pellets was determined by the variability of the TL signal study obtained from the samples treated at 300 °C for 1 h and not irradiated. The minimum doses were 7.0 and 4.0 Gy to the first and second TL peaks, respectively, by calculating three times the standard deviation shown in five samples.

4. Conclusions

This preliminary study shows that the glass transition point of the Teflon® is at about 48 °C and the melting point at 340 °C. Teflon acts as an agglutinator, giving greater strength to the pellets due to the fibers stretching during the sintering process.

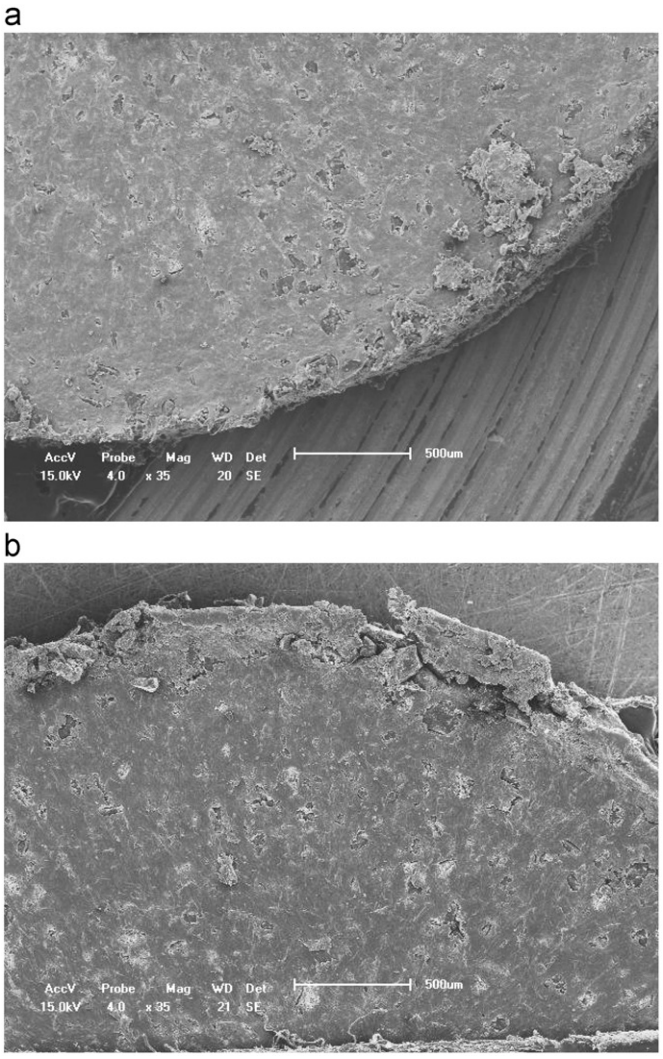

Fig. 4. Micrographs of spodumene/Teflon® pellets, both with increase of 35 ×.

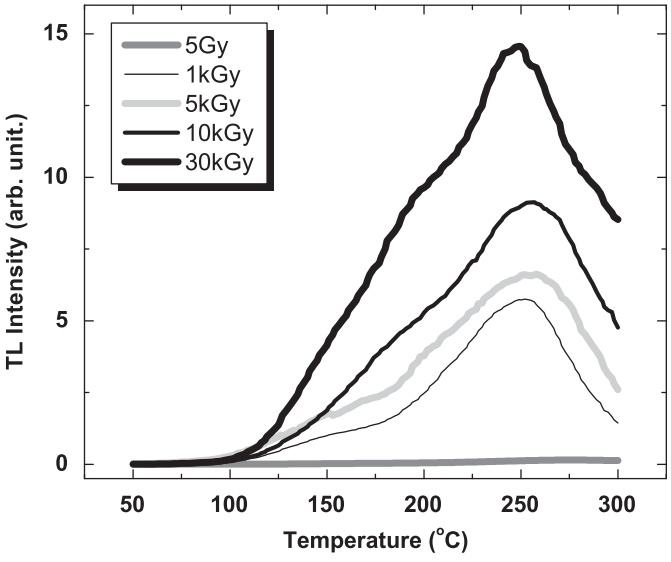

Fig. 5. Glow curves of pure Teflon pellets irradiated with ^{60}Co.

However, the TL response of pure Teflon pellets may influence high-dose dosimetry when it is applied as agglutinator in TL materials.

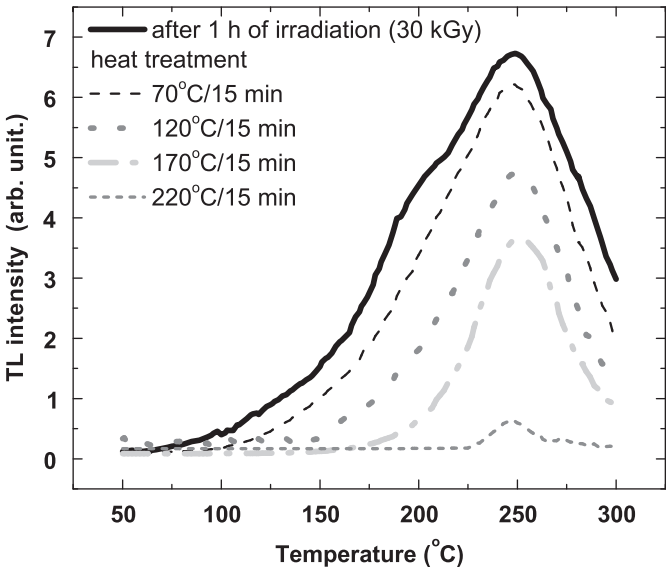

Fig. 6. Glow curves of Teflon pellets, 1 h after irradiation (30 kGy of ^{60}Co) and after different temperatures of thermal treatments.

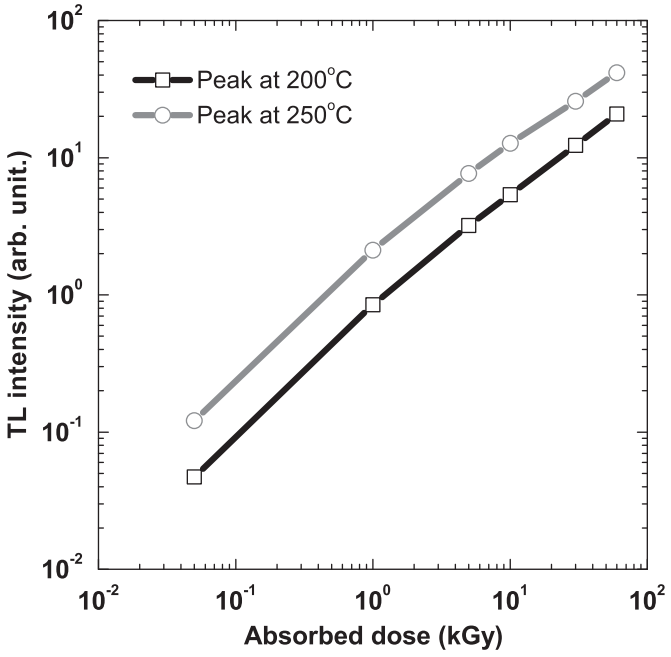

Fig. 7. Dose–response curves of the Teflon pellets irradiated with ^{60}Co. Measurements performed 1 h after irradiation.

The dosimetric properties of pure Teflon pellets indicate the possibility of their application in high-dose dosimetry as TLDs. The use of Teflon as a dosimetric material has the advantages of low cost, easy preparation and handling.

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