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Thermoanalytical study of polyurethane, subjected to ionizing radiation, as raw material for catheters for clinical practice

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Abstract The present work aimed to study the thermal behavior of commercial polyurethane catheters before and after irradiation, in order to characterize the polymeric material of these catheters. Fourier transform infrared spectroscopy (FTIR) enabled the identification of functional groups in the structure of macromolecules, such as poly(esterurethane) and poly(etherurethane) in catheters of various origins, and it was confirmed that is a poly (etherurethane) sample. DSC and TG were employed to observe the changes in the properties of the material before and after degradation. DSC curve at the constant heating and cooling rate allowed the characterization of thermal properties, such as T_m and T_g of copolymers, as well as highlighting the main thermal events. TG provided T_{onset} and $T_{peak\ DTG}$, where it was possible to evaluate the thermal degradation and the mass loss of the polymer, resulting from a physical transformation such as evaporation or chemical as degradation, in a continuous process as a function of temperature. The comparative assessment conducted between the catheters before and after irradiation by FTIR, Raman and DSC enabled the use of radiation as agent of sterilization.

Keywords Polyurethane catheters · Thermal analysis · Ionizing radiation

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Introduction

Central venous catheters (CVC) are normally employed in critical patients to administer fluids, blood products and parenteral nutrition. The use of these devices is associated with the most infections of the bloodstream.

Development of catheters coated with silver nanoparticles aims to reduce current infection rates of these catheters in clinical practice, justifying the study of characterization of these commercial polyurethane catheters and evaluating the surface adhesion of the coating.

As a general objective, the survey focuses on the characteristics of polyurethane for thermal analysis and the study of the use of ionizing radiation in commercial catheters of this material. Also, the goal is the development of manufacturing methods and characterization of catheters coated with antimicrobial materials and preventive action to the formation of biofilm. Search relates these catheters to the coating surface features depending on the action of ionizing radiation, exploring potential benefits arising from the control of surface properties.

The knowledge of the thermal behavior of materials is decisive for the manufacture and processing of a wide variety of polymers. The technique of differential scanning calorimetry (DSC) is predominant for polymers and allows the investigation of thermal effects, such as fusion, cristalinização, cross-linking, glass transition, specific heat and oxidation. On the other hand, the thermogravimetry

(TG) provides information about the composition, thermostability, thermal degradation and oxidation of polymer blends and blends.

DSC is used extensively in the characterization of polymers and quality control, both in research laboratories and industry [1]. When you want to compare results, it is appropriate to ensure that all samples have the same thermal history; this can be done by an identical procedure for all samples [2]. DSC also allows the determination of the melting temperature (T_m) and the glass transition temperature (T_g) of the polymer and can also be used to distinguish a block copolymer (AAABBB) from a random copolymer (ABAABAB), whereas for the block copolymer are observed two T_g values, as random copolymers exhibit only one T_g values.

TG is a technique widely used in thermal degradation profile of polymers as well as other materials. Exposure to high temperature can sometimes change the chemical structure and, consequently, the physical properties of materials. Therefore, TG curve in non-isothermal conditions shows the profile of resistance or thermal stability that the material presents when subjected to a linear variation in temperature. Thermal stability is defined as the ability of the substance to maintain their properties as close as possible to its initial characteristics and needs to be considered in terms of the environment imposed on the material and the functions it should perform.

The first-derivative TG curve (DTG curve) allows to define with greater clarity the initial and final temperature of a particular step of mass loss; the number of peaks is consistent with the number of steps of mass loss and also allows the separation of overlapping events. The temperature indicated by the DTG peak ($T_{peak\ DTG}$) shows the point where the event is occurring more quickly. Also, the peak width indicates how quickly or slowly a thermal process occurs in relation to another.

The polymers when subjected to a heat treatment may include structural changes characterized by breaking chemical bonds in the main and side chains. These changes are evidenced by the decrease in molar mass releasing volatile products [3].

According to the studies conducted by Jiang [4], the thermal degradation behavior of polyester polyurethane and polyether polyurethane was investigated in different environments by means of TG/DTG curves in the range of temperature of 20–700 °C. The association of the results of TG/DTG with those of fourier transform infrared spectroscopy (FTIR) showed that the poly(esterurethane) and poly(etherurethane) features two stages of thermal degradation under air atmosphere, but for polyether polyurethane, degradation occurs in just one step. The results of TG/DTG showed also that the initial degradation temperature extrapolated (T_{onset}) poly(etherurethane) is smaller than that of poly(esterurethane), suggesting that the thermal stability of the first polyurethane is greater than the second polyurethane. It was also observed that the T_{onset} of the heated samples under air atmosphere is less than N_2 atmosphere, suggesting that the presence of O_2 affects significantly the breaking of polymer chains [4].

Conforming to studies conducted by Hung [5], poly (etherurethane) (PEU) ($T_{peak\ DTG} = 402.6$ °C), are data obtained by thermogravimetry of PEU and PEU nanocomposites—Ag, performed with a thermogravimetric analyzer (TGA2050; TA Instruments, New Castle, DE). The glass transition temperature ($T_g = -72.3$ °C) was determined using a cell DSC model SSC/5200 (Seiko, Tokyo, Japan) [5].

Polyurethanes are commonly employed for obtaining catheters; therefore, studies of these catheters are primordial, as one of the biggest challenges of treating severely ill patients, by contamination of same when introduced into the bloodstream, and subsequent infection, severe sepsis and septic shock, associated with high morbidity and mortality [6].

The type of catheter material is related to adhesion and greater ease of biofilm formation [7]. In vitro studies showed that polyvinyl chloride or polyethylene catheters are more susceptible to microbial adherence than those of polyurethane.

Suggestions for vascular access prevention, among others, such as catheters coated with silver nanoparticles, with high performance, because of advances in nanoscience and nanobiotechnology, it would be the method for developing catheters with differentiated characteristics in their applications and specific qualities [8].

Usually, these catheters are sterilized with ethylene oxide, and one of its manufacturers is the Biomedical Equipment and Medical-Surgical Products Ltd [9]; however, by the use of ionizing radiation, obtaining these sterilized catheters would be a viable possibility.

Ionizing radiation can cause changes in the physical and chemical properties of plastics materials [10] such as splitting and cross-linking [11], and it also causes effect on the crystal lattice, determining changes in polymer properties, and formation of gases and radiolysis products, with increased or decreased molar mass and forming a three-dimensional network.

The nature and extent of chemical and physical changes in polymers induced by ionizing radiation are influenced by the following factors: O_2, antioxidants, stabilizers and slip agents, which are added to the polymer to improve its performance and other additives. The O_2 present during irradiation can lead to oxidative cleavage of the polymer chain and oxidation of the polymer, leading to formation of peroxides, alcohols, carbonilics fractions and monoxides and dioxides carbon and several compounds containing oxygen, with low molecular weight.

Economically viable irradiation processes for industrial application, such as radiation from high-energy electrons (electrons accelerated), which is called electron beam ("electron beam"), which are generated in particle accelerators devices (electron accelerators) [12]. They were used to study the effect of radiation in the polymer.

The great advantage of using the irradiation process is non-use of additives, meaning a clean process; furthermore, the product obtained already gets sterilized.

Experimental

Material

Polyurethane, PU, used in this work is present in central venous catheters (CVC), JOHNSON & JOHNSON [13]. The supplier of catheters is the Biomedical equipment and Medical-Surgical Products Ltd [9], which were not submitted to previous treatment before the characterization.

Methods

Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) were registered in the PerkinElmer spectrometer, Spectrum Model One, coupled with universal device ATR ("Sampling Accessory"), employing solid samples and wavelength spectral range from 500 to 4000 cm^{-1}. The equipment has a comparison program that allows to correlate the spectral differences occurred between the samples analyzed.

Thermogravimetry and derivative thermogravimetry (TG/DTG)

TG/DTG curves were obtained by employing the thermobalance model TGA-51 (Shimadzu), in the temperature range 25–900 °C, under dynamic air atmosphere (50 mL min^{-1}), heating rate 10 °C min^{-1} and Pt crucible containing approximately 5 mg of sample. Before experiment, blank curve was obtained to assess the baseline system. The calibration of TGA-51 equipment was conducted according to ASTM (1582-04). Verification of the conditions of measures was carried out using a standard of calcium oxalate monohydrate with 99.99 % purity, origin Merck.

Differential scanning calorimetry (DSC)

DSC curves were obtained using the DSC cell model DSC-50 (Shimadzu), under a dynamic N_2 atmosphere (100 mL min^{-1}) in the temperature range −100 to 600 °C, heating rate 10 °C min^{-1}, in Al partially enclosed crucible containing approximately 2 mg of sample. Before the experiments were obtained blank curves to evaluate the baseline system under the same conditions of the measures, however, without the use of capsules of sample and reference. The cell DSC was calibrated before the experiments, using standard substances indium ($T_{fusão}$ = 156.6 °C; $\Delta H_{fusão}$ = 28.7 - J g^{-1}) and zinc ($T_{fusão}$ = 419.5 °C), metal purity 99.99 %.

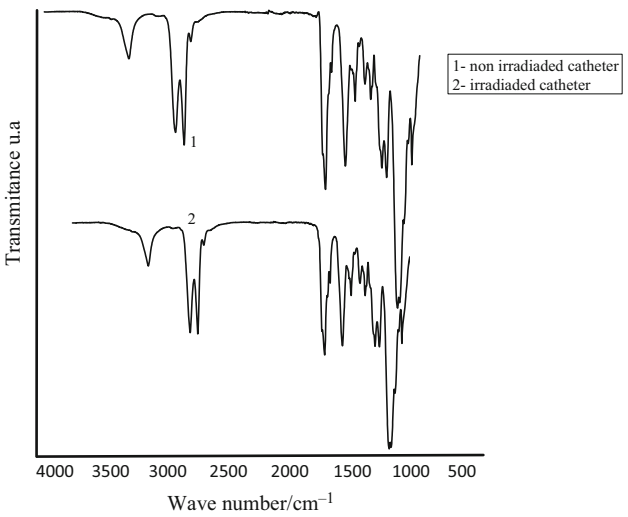

Fig. 1 FTIR non-irradiated and irradiated catheter spectra

Scanning electron microscopy (MEV/EDS)

The experiments were conducted in a scanning electron microscope of PHILIPS-EDAX 20 kV, the Center of Science and Technology of Materials (CCTM) of IPEN-CNEN/SP.

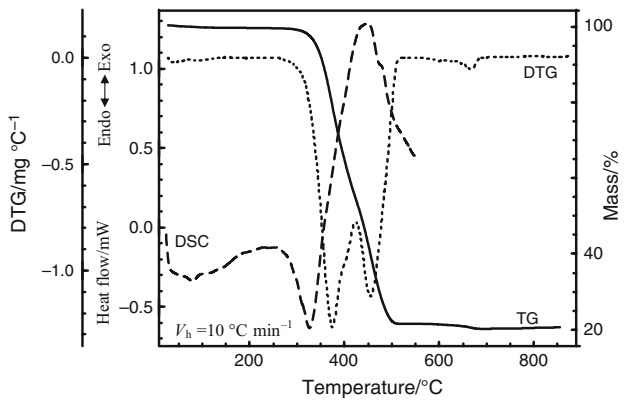

Fig. 2 TG/DTG and DSC curves obtained at 10 °C min^{-1}, under dynamic air atmosphere and employing about 15 mg (TG/DTG) and about 2 mg (DSC) sample of non-irradiated catheter

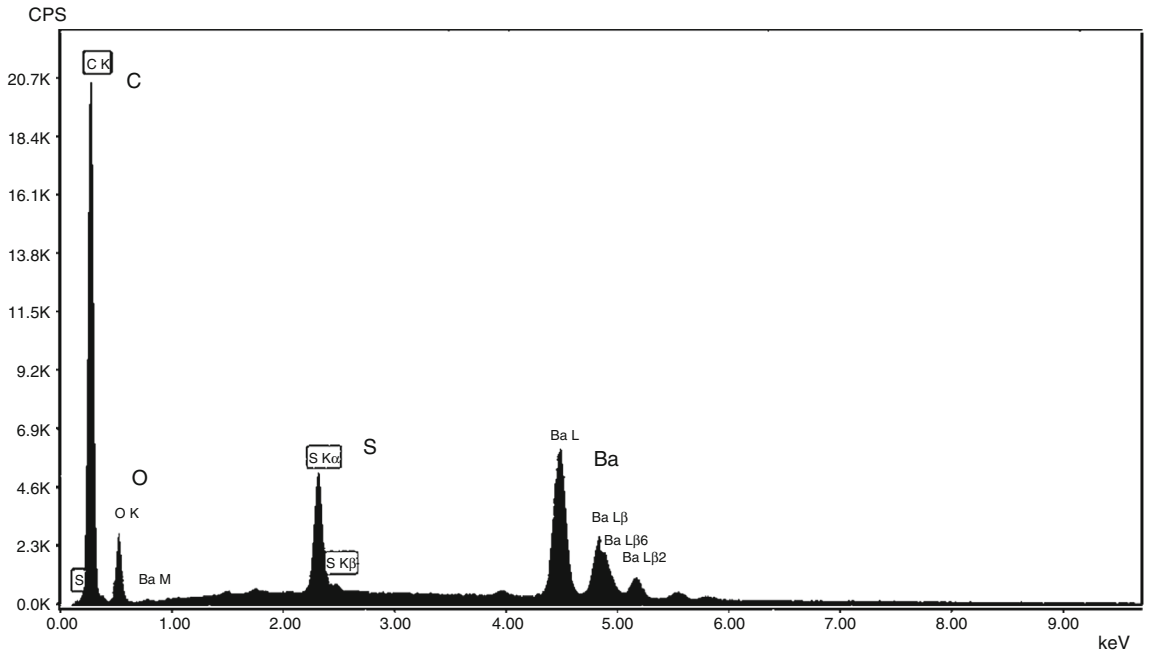

Fig. 3 EDS non-irradiated catheter

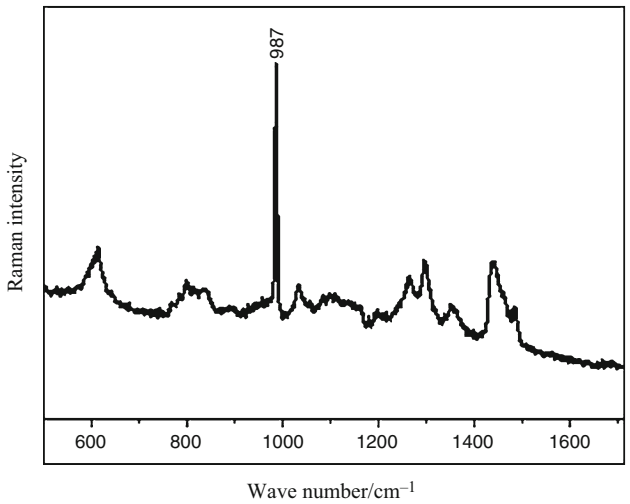

Fig. 4 Raman non-irradiated catheter spectra for sulfate group identification

Raman spectrometry

The spectra were registered on a micro-Raman spectrometer Renishaw InVia Reflex, with type detector CCD (*charge-coupled device*), Molecular Spectroscopy laboratory, Institute of Chemistry, the University of São Paulo-IQUSP.

Table 1 Results of TG/DTG and DSC of the catheter and PEU poly(etherurethane)

Materials	DTG	DSC	
	T_{peak}/°C	T_g/°C 1 cycle	T_g/°C 1 cycle
Catheter	375	−72.1	−70.5
	456		
PEU*	402.6	−72.3	

* means data extracted from [5]

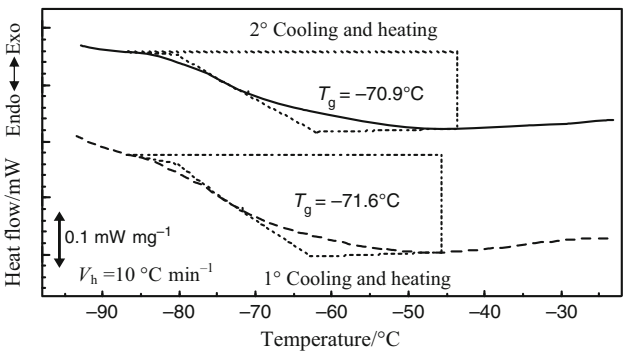

Fig. 5 DSC curves obtained at 10 °C min^{-1}, under a dynamic N2 atmosphere of non-irradiated catheter samples in the temperature range from −100 °C to 120 °C

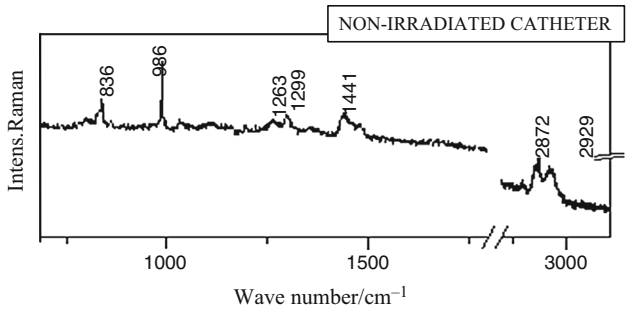

Fig. 6 Raman non-irradiated catheter spectra

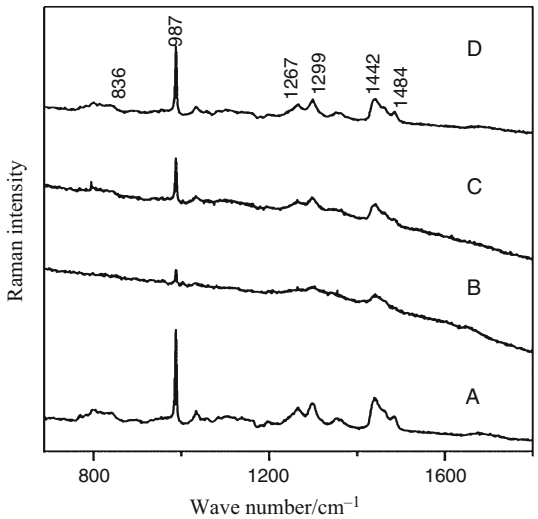

Fig. 7 Raman irradiated catheter spectra

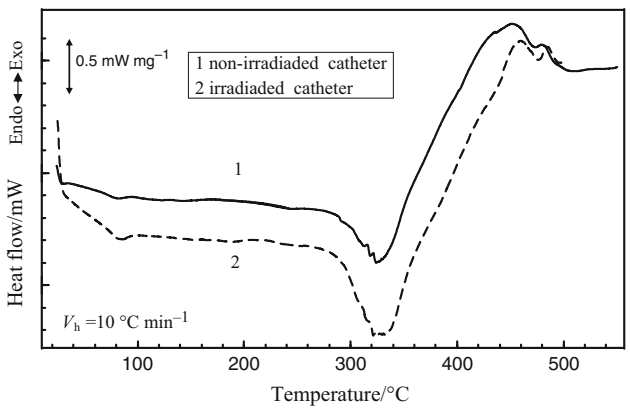

Fig. 8 DSC curves obtained at 10 °C min^{-1}, under a dynamic N2 atmosphere of non-irradiated and irradiated catheter samples

Irradiation of samples

The samples were irradiated with electron beam using an electron accelerator Dynamitron JOB 188 power 0.5–1.5 MeV and 0.3–25 mA current, the Technology Center of Radiation of IPEN-CNEN/SP, subjected to radiation dose of 25 kGy, used for sterilization of materials, and

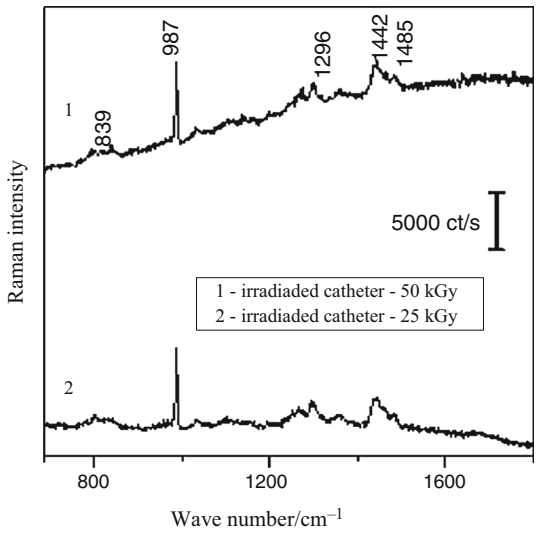

Fig. 9 Raman spectra catheter irradiated at doses of 25 and 50 kGy

then characterized by DSC, FTIR and Raman, with subsequent analytical comparison with non-irradiated catheters.

Results and discussion

Fourier transform infrared spectroscopy (FTIR) polyurethane non-irradiated catheter illustrated in Fig. 1 shows the main bands in 1090 cm^{-1}, (C–O–C) ether group; 3400 cm^{-1}, stretching, ν (NH) urethane; and 1700 cm^{-1} to stretch, ν (C=O) group urethane, and it leaves no doubt which is a poly(-etherurethane) sample [4]. In addition, FTIR polyurethane irradiated catheter illustrated in Fig. 1 shows the main bands in 1091 cm^{-1}, (C–O–C) ether group; 3318 cm^{-1}, stretching, ν (NH) urethane; and 1693 cm^{-1} to stretch, ν (C=O) group urethane. Therefore, significant changes were not observed in poly(etherurethane) [4].

Figure 2 illustrates TG/DTG and DSC curves non-irradiated catheter sample. TG/DTG curves showed mass loss 0.8 % between 25 and 150 °C due to the elimination of moisture water, identified in the DSC curve at endothermic event with T_{peak} at 79.3 °C. The material is thermally stable up to approximately 310 °C and decomposes between 310 and 500 °C with 79 % mass loss and with $T_{peak\ DTG}$ in 375 and 455 °C, which indicates that the process occurs in two steps. Indeed DSC curve also showed two thermal events, endothermic and exothermic, in the same temperature range ($T_{peak\ DSC}$ in 327 and 449 °C). The TG/DTG curves still showed another loss of mass between 550 and 700 °C of 1.3 % that may be associated with the thermal decomposition of some inorganic material employed as filler on polymer matrix, or burning carbonaceous material formed in the previous steps. In addition, the temperature of 900 °C has a residue that represents 20 % of the initial mass.

This corresponds to residue barium sulfate employed as inorganic filler for obtaining the catheter. The presence of barium was identified in the sample of the catheter non-irradiated by EDS measures (Fig. 3), while the sulfate by Raman spectroscopy [14] (Fig. 4); the intense band at 987 cm^{-1} corresponds to the symmetric stretching of this group from the barium sulfate, used as filler in polymers.

Table 1 lists the comparison of temperatures reached at DTG curve (Fig. 2) from the sample of poly(etherurethane) employed as catheter, with temperatures reported in the literature [5] for sample of similar material.

DSC experiments were conducted to enlarge the sample characterization. Figure 5 shows DSC curves obtained for the sample of non-irradiated catheter subjected to two cycles of cooling/heating. These experiments were conducted in the temperature range −100 to 120 °C, using liquid N_2, for the determination of glass transition temperature (T_g) of the polymer matrix. Figure 5 illustrates DSC curves obtained for the sample of non-irradiated catheter subjected to two cooling/heating cycles. The T_g values obtained in the first and second cycle are listed in Table 1 and the T_g value of a sample of PEU according to Ref. [5]. The values are concordant, leaving no doubt that this is a poly(etherurethane).

Bands are expected related to polyurethane in higher frequency Raman region at 2872 and 2929 cm^{-1} correspond to symmetric and asymmetric stretches CH, the symmetrical stretching of this group in 1442 cm^{-1} in non-irradiated catheter is present in Raman spectrum, illustrated in Fig. 6 and it also was shown in irradiated catheter in Fig. 7 which could be observed four point (A–D) analyzed on the sample. In addition, sample showed a uniformity because the Raman spectrum has different relative intensity bands and maintain frequency values constant [15].

In Figs. 6 and 7 are shown Raman spectra non-irradiated catheter and irradiated catheter, and in Fig. 9 is presented Raman spectra irradiated catheter comparing doses of 25 and 50 kGy.

In Fig. 8, to complement the evaluation of the ionizing radiation influence on the catheter, the sample irradiated have kept the same conditions of the non-irradiated catheter to be characterized by DSC. In the result shown in Fig. 8 it was possible to conclude that the radiation dose employed did not cause significant changes in catheter. Therefore, spectrum Raman, Figs 6, 7, 9 and FTIR, Fig. 1, of the catheter irradiated sample and the non-irradiated catheters did not showed any modification.

Conclusions

Evaluation of the thermal behavior of polymeric materials from mass losses obtained in TG/DTG curves and the determination of the T_g by DSC enable a prior knowledge and essential of a polymer to be used in health care. Thus, the association of thermoanalytical results, FTIR and Raman spectra of non-irradiated and irradiated materials with ionizing radiation from high-energy electrons (accelerated electrons) extended the knowledge to define this form of sterilization which presents the advantage of being a clean process.

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