Evaluating structural and microstructural changes of PDMS-SiO₂ hybrid materials after sterilization by gamma irradiation

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Abstract

PDMS-SiO₂ hybrid materials obtained by sol-gel process has been extensively studied over the past years due to its promising biomedical applications namely as bone substitutes, catheters, drug delivery devices, etc. Regardless the intended biomedical application, all these materials should go through a sterilization process before interfacing a living structure. However, it is unclear whether they undergo structural and microstructural changes when subjected to sterilization by gamma irradiation. This paper addresses this issue by showing that a sol-gel processed biomaterial based on the PDMS-CaO-SiO₂ hybrid system suffers only small structural changes when submitted to a radiation dose of 25 kGy, the dose usually recommended to achieve a Sterility Assurance Level of 10⁻⁶ when the natural contamination level and microorganism types cannot be calculated. The characterization was assessed by FT-IR, ²⁹Si-{¹H} CP-MAS, thermal analysis (DTG), and SEM.

1. Introduction

The development of hybrid materials is one of the fastest areas of research in the world due to their wide range of possible applications [1] namely as biomaterials [2], anti-corrosion coatings [3] and as surface modifiers of fabrics [4]. From the earlier works of Tsuru *et al.* [5], hybrid materials based on the polydimethylsiloxane (PDMS) – tetraethyl orthosilicate (TEOS) system, prepared by sol-gel, have been pointed out as potentially bioactive when calcium is added to the composition [6,7]. Their original idea, was to obtain a bioactive hybrid material, named “ormosil” (organically modified silicate), with mechanical properties similar to those of the human bone, where the inorganic domains are mainly SiO_4 structural units and the organic ones $(\text{CH}_3)_2\text{SiO}_2$ structural units. Recently, PDMS- SiO_2 based hybrid materials, prepared by sol-gel, have been widely explored for the production of scaffolds for bioreactors [8,9], tissue engineering applications [10,11] and drug delivery systems [12,13].

The sterilization of a biomaterial through gamma radiation has advantages over the ethylene oxide method since it does not leave any residues and is compatible with most materials [14]. However, it is well known that gamma radiation may induce the formation of reactive species whose effects propagate over time [15]. For example, radiation effects in polymers promote crosslinking and scissioning [14], and high radiation doses can cause brittleness and cracks on the material's surface [16]. The authors themselves [17,18] have used high dosages of gamma-ray irradiation (200 to 5000 kGy) to produce PDMS- SiO_2 - ZrO_2 hybrids using metal alkoxides and high molecular weight hydroxyl terminated PDMS as precursors, proving that high doses of gamma radiation is effective to promote PDMS crosslinking as well as the linking between PDMS domains and metal oxide domains.

To the best of our knowledge, a study about the effects of ionizing radiation used for sterilization on the structure of hybrid materials prepared by sol-gel based on the system PDMS- SiO_2 have not yet been made.

This work aims at the evaluation of structural and microstructural modification induced by gamma radiation in PDMS- SiO_2 hybrid materials prepared by sol-gel. A simple PDMS- SiO_2 and a bioactive PDMS- SiO_2 -CaO hybrid materials obtained by sol-gel previously studied [19] were subjected to a gamma radiation dose of 25 kGy, the dose usually recommended [20] [21] to achieve a Sterility Assurance Level (SAL) of 10^{-6} (the probability of a micro-organism to survive

after the process) when the natural contamination level and microorganism types cannot be calculated. The structure of both hybrids, before and after the sterilization, were characterized by FT-IR and $^{29}\text{Si}\{-^1\text{H}\}$ CP-MAS, the thermal behaviour was assessed by thermogravimetry (DTG), and the microstructures observed by SEM.

2. Materials and methods

2.1 Material preparation and sterilization

Tetraethylorthosilicate (TEOS), polydimethylsiloxane (PDMS) silanol terminated (550 g mol^{-1} average molecular weight), calcium acetate monohydrate ($\text{Ca}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$), isopropanol (IPA) and HCl (25% solution), all from Sigma-Aldrich, were used as raw materials for the preparation of the hybrids. The compositions of the materials are presented in Table 1. TEOS was first added to PDMS and H_2O and then to a aqueous solution of $\text{Ca}(\text{CH}_3\text{CO}_2)_2$. Afterwards, IPA was put together and the medium was acidified with HCl. The final mixtures samples were stirred for 5 hours and poured into 22 mm diameter polypropylene containers. Samples were aged for 24 h at room temperature and then placed in an oven at 60°C during 7 days for gelation. After that the obtained gels were dried at 150°C for 24 h giving rise to handleable monolithic cylinders. The dried samples were cut into disks with a diameter of ca. 15 mm and thickness of ca. 1.5 mm, separated in different bags and sealed in a N_2 atmosphere. Then, they were irradiated at the ^{60}Co irradiation facility, UTR, [20] located at CTN/IST, using an average dose rate of 9.602 kGy h^{-1} until the total dose of 25 kGy was achieved.

2.2. Material characterization

Samples were pulverized in a mortar in order to create thin powders and were analysed by FT-IR spectroscopy (Mattson 7000) and by solid-state $^{29}\text{Si}\{-^1\text{H}\}$ cross-polarization-magical angle spinning (CP-MAS) NMR (Bruker Avance 400). Pellets were prepared for FT-IR measurements by mixing and grinding a small quantity of powder with spectroscopic grade dried KBr powder and the spectra were recorded with a 4.0 cm^{-1} resolution in the $4000\text{--}350 \text{ cm}^{-1}$ range. $^{29}\text{Si}\{-^1\text{H}\}$ CP-MAS NMR essays were carried out, with a ^1H 90° pulse width of $4.75 \mu\text{s}$, a delay time of 5 s, and a CP contact time of 8 ms. The CP-MAS spectra were simulated (not shown) using DMFIT software [22]. Data from the literature [23–26] was used to simulate the peaks assigned

to difunctional D ((CH₃)₂.SiO₂ and tetrafunctional Q (SiO₄) structural units. Thermal behaviour of the samples was assessed by thermogravimetry (TA instrument model 951). The assays were carried out under a nitrogen atmosphere from 22 to 700 °C, using a 10 °C min⁻¹ heating rate and data was analysed using TA Universal Analysis 2000 software. Derivative thermogravimetric (DTG) curves were calculated. Microstructure observation of fracture surface was performed by SEM (Hitachi S4100) with an accelerating voltage of 25 kV.

Table 1: Compositions of samples

Notation	Composition (in molar ratio)				
	TEOS	PDMS	H ₂ O	HCl	Ca
Ca0	1	0.18	5	0.225	0
Ca10	1	0.18	5	0.225	0.10

3. Results and discussion

3.1. FT-IR analysis

The FT-IR studies were performed in the 300-4000 cm⁻¹ range on samples of both Ca0 and Ca10 compositions. The results obtained for samples before and after being sterilized with a 25 kGy gamma radiation dose as shown in Figure 1.

All samples exhibit bands in the 569-3469 cm⁻¹ region, previously reported by other authors [27–29] as characteristic of PDMS and sol-gel processed silica. As an example, the bands at ca. 2965, 1420 and 1260 cm⁻¹, are assigned to asymmetrical C-H stretching, asymmetrical, and symmetrical bending of CH₃ groups, from PDMS.

The presence of bands at ca. 565 and 430 cm⁻¹, observed in silica-gels [30] and PDMS-SiO₂ based hybrid materials [27,31], are assigned respectively to Si-O-Si vibration in 4-fold siloxane rings and bending mode of O-Si-O bonds.

The bands at ca. 430 cm⁻¹ and 850 cm⁻¹ present in all samples, before and after sterilization, were attributed to the presence of hybrid cross-linked SiO₂ (Q units) – PDMS (D units)

structures [27,29]. The first frequency value, downshifted when compared to values obtained for pure silica gel (usually near 460 cm^{-1}), has been reported to the continuous interruption of silica network with hybrid $\text{SiO}_4-(\text{CH}_3)_2\cdot\text{SiO}_2$ linkages. Similarly, the presence of hybrid bonds can also explain the downshift of the frequency assigned to the symmetrical rocking of CH_3 groups. Pure PDMS chains exhibit a weak band at 860 cm^{-1} , assigned to the symmetrical rocking of CH_3 groups, that shifts to lower values in co-polymers containing Q structural groups. A slight upshift from 426 cm^{-1} to 430 cm^{-1} is observed for the base Ca0 composition upon sterilization indicating a possible break of some hybrid D-Q linkages; the same effect is not observed in the Ca-containing samples Ca10.

Slight differences are also observed in the “*shape*” of the region between 1000 and 1250 cm^{-1} after sterilization, for both samples. Once this region is assigned to asymmetric stretching of Si-O-Si bonds in both D and Q groups, those differences can indicate some variations in the geometry and size of the siloxane condensed species [28,32].

The existence of adsorbed water, more evident in the Ca- containing samples, is observed in both compositions, even after sterilization, as confirmed by the presence of the bands at ca. 3450 cm^{-1} and 1640 cm^{-1} assigned respectively to the deformation and bending vibrational modes of O-H bonds [28].

Fig. 1. FTIR spectra of hybrid samples with (Ca10) and without (Ca0) calcium in the composition for both non-irradiated and irradiated at 25 kGy samples.

No C-O vibrational modes, common in acetate based materials, were detected by FT-IR spectroscopy. This can be attributed to the protonation of the carboxylic group of calcium acetate in the highly acidic medium used in the synthesis, leading to the formation of acetic acid. In turn, the acetic acid reacts with the excess 2-propanol present in the solution originating an ester (2-propyl ethanoate), which has a boiling point lower than the temperature at which the materials were subjected [33].

3.2. Solid-state $^{29}\text{Si}\{-^1\text{H}\}$ CP-MAS NMR analysis

$^{29}\text{Si}\{-^1\text{H}\}$ cross-polarization-magical angle spinning NMR (CP-MAS NMR) is being used as a valuable technique to study PDMS-SiO₂ based hybrid systems due to the presence of protonated groups directly bonded to some Si structural units [34,35]. It is known, from previous works [36,37] and from the literature [35], that the lack of efficiency of the cross-polarization

(CP) sequence for the signal due to high mobile D units inside very long PDMS chains, is compensated by the existence of more constrained D structural units in short chains (1 to 3 monomers) linked to Q units or hydroxyl groups, thus justifying the choice of the CPMAS. Figure 2 shows the $^{29}\text{Si}\{-^1\text{H}\}$ CP-MAS spectra for both studied compositions before and after being irradiated. Very few differences can be observed after sterilization. A loss of signal from inner D structural groups of long (more than 5 monomers) PDMS chains in the region near -22 ppm is evidenced by the disappearance of the sharp peak observed in Ca0 after irradiation, probably indicating breakage of those chains. This effect is not evident in the Ca-containing composition. This seems to be in good agreement with the results from FT-IR.

Some slight differences are also observed, in both irradiated compositions, in the regions usually assigned to the presence of a terminal D unit with a hydroxyl group linked to a PDMS chain (near -12 to -13 ppm, $\text{D}_{\text{OH}}^1 - \text{D}^2$) or linked to a silica domain (near -9 to -10 ppm, $\text{D}_{\text{OH}}^1 - \text{Q}^4$) [38,39].

Fig. 2. NMR spectra of hybrid samples with (Ca10) and without (Ca0) calcium in the composition for both non-irradiated and irradiated at 25 kGy samples.

3.4. Thermal analysis

The thermal behaviour of the hybrid samples with and without Ca in the composition was studied from 22 °C to 700 °C. Figure 3 shows the derivative thermogravimetric curves (DTG) for these materials.

It is clear that the Ca-containing hybrid samples (Ca10) exhibit a thermal behaviour that is different from the one shown by the Ca-free composition (Ca0). In samples Ca10 the DTG plots illustrates an abrupt weight loss up to 110 °C associated to water release during the heating process [36]. Calcium is well known for its high hygroscopic capacity, being able to establish bonds with OH molecules in the preparation bath creating a kind of solvation sphere around it [40]. These OH molecules are present in the water added to the preparation mixture in the Si-OH groups of the PDMS chain ends, as well as in the atmospheric water.

Fig. 3. Derivative thermogravimetric (DTG) plots of hybrid samples with (Ca10) and without (Ca0) calcium in the composition for both non-irradiated and irradiated at 25 kGy samples.

Camino *et al.* [41] described the thermal degradation of PDMS as a two stages process: a first weight loss near 300 °C attributed to decomposition of the PDMS, forming cyclic oligomers (mainly hexamethylcyclotrisiloxane) through Si–O bond scission and resulting in a chain folded cyclic conformation (which is energetically more favourable) and a second weight loss related to the final decomposition of those cyclic oligomers, which occurs above 400 °C. In the present study this two-stage process is only clearly observed in the calcium containing composition. It is possible to verify that the temperature attributed to the degradation of PDMS decomposition [41] of the Ca10 samples is always higher when compared to that of the Ca0 samples, either without radiation (0 kGy) or upon 25 kGy radiation. This is an indication that the introduction of Ca in the hybrid composition may lead to a thermal stabilizing effect in these materials. Moreover, if we compare the degradation temperature in the Ca10 samples at 0 kGy and 25 kGy dose we observe that the degradation temperature of Ca10 at 25 kGy is slightly higher. It seems that the radiation increases the thermal resistance of these materials, probably due to some rearrangement of the siloxane condensed species.

3.5 SEM observations

The representative microstructure of the samples Ca0 and Ca10 at 0 kGy and 25 kGy is shown in Fig. 4.

Fig. 4. SEM micrographs of the hybrid samples with (Ca10) and without (Ca0) calcium in the composition for both non-irradiated and irradiated at 25 kGy samples.

After a careful observation of the microstructural characteristics (eg. the size of porosity) of both Ca0 and Ca10 materials, it is possible to conclude that the irradiation of these materials at 25 kGy induces no perceived changes in the microstructure.

4. Conclusions

Hybrid materials of the PDMS-SiO₂ system with and without calcium in the composition were prepared through the sol-gel method. Discs of these samples were subjected to a gamma radiation dose of 25 kGy. The characterization of these materials, before and after irradiation,

was assessed by FT-IR, $^{29}\text{Si}\{-^1\text{H}\}$ CP-MAS, thermal analysis (TGA and DSC), and the microstructures were observed by SEM.

It was found that radiation induces no relevant changes in the structure and microstructure of these materials. Moreover, both the addition of calcium to the composition and the irradiation at 25 kGy contribute for the improvement of the thermal stability of these materials.

This work shows that PDMS-SiO₂ hybrid materials are suitable to undergo a sterilization process by gamma irradiation while preserving the structure and microstructure of the materials as-processed and even increasing its thermal stability .

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