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Evaluation of the effect of a therapeutic dose of gamma irradiation on the thermal and structural properties of polycaprolactone/gypsum composite films

Avaliação do efeito da irradiação gamma em dose terapêutica nas propriedades térmicas e estruturais em filmes do compósito policaprolactona/gesso

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ABSTRACT
In this study, the effect of a therapeutic dose of gamma irradiation used, for example, in cancer treatment, on the thermal and structural properties of polycaprolactone/gypsum composite films (PCL/Gesso Cs) was evaluated. The composite films (Cs) were obtained by the solvent evaporation method, using chloroform as a solvent, and were irradiated at 140 Gy in the presence of air at room temperature. Then the films were characterized by experimental techniques such as: Infrared Spectroscopy (FT-IR), Thermogravimetric Analysis (TGA), X-Ray Diffraction (DRX) and Scanning Electron Microscopy (SEM). Previous results demonstrated that gamma irradiation at the evaluated dose changed the thermal properties of composites.

Keywords: Polycaprolactone, Gamma Irradiation, Gypsum, Thermal properties.

RESUMO
Neste estudo, foi avaliado o efeito de uma dose terapêutica de irradiação gama utilizada, por exemplo, no tratamento do câncer, nas propriedades térmicas e estruturais de filmes compostos de policaprolactona / gesso (PCL / Gesso Cs). Os filmes compósitos (Cs) foram obtidos pelo método de evaporação de solvente, utilizando clorofórmio como solvente, e foram irradiados a 140 Gy na presença de ar à temperatura ambiente. Em seguida, os filmes foram caracterizados por técnicas experimentais como: Espectroscopia de Infravermelho (FT-IR), Análise

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Termogravimétrica (TGA), Difração de Raios X (DRX) e Microscopia Eletrônica de Varredura (MEV). Resultados anteriores demonstraram que a irradiação gama na dose avaliada alterou as propriedades térmicas dos compósitos.

Palavras-chave: Policaprolactona, Irradiação Gama, Gesso, Propriedades térmicas.

1 INTRODUCTION

Gypsum is a low-cost ore derived from calcination of gypsite with a chemical structure $CaSO_4.0.5H_2O$ (calcium sulphate hemihydrate) [1]. However, around 96% of the gypsum obtained from gypsite is used in the civil construction sector [1]. Other applications of lesser use for gypsum include its use in the production of paper, the orthopedic industry, dental sector, as fillers for polymeric materials, among others [1]. The use of gypsum has been highly researched to obtain new materials. The use of gypsum as filler in polymers has applications in the biomedical sector [2,3], given that gypsum is considered a biomaterial generally safe and without adverse reactions [4]. However, gypsum does not have satisfactory bioactivity, making it difficult to use alone, which is not favorable to biomedical applications such as bone regeneration [5]. This justifies its use in the formation of biocompatible polymer composites for these applications [5], combined with its performance as filler for polymers. Zhang and co-workers have reported on the use of simvastatin with silicate/gypsum and gelatin for the design of a bone substitute aimed at bone growth[5]. A study reported by Low and co-workers revealed the potential of a composite formed by gypsum and chitosan for coating dental pulp [6]. These studies demonstrate the use of gypsum in polymeric composites for implants. Polycaprolactone is among the polymers that can be used to obtain composites with gypsum. Polycaprolactone is a thermoplastic, hydrophobic, semi-crystalline, bio-compatible and biodegradable polymer [7,8]. Various composite materials have been obtained from polycaprolactone for biomedical applications such as in drug delivery [9], tissue engineering [10], gene therapy [11], and implants [12]. Gatta and colleagues produced an injectable system from PCL with $CaSO_4.0.5H_2O$ for applications in the dental and orthopedic sector [13]. Mallakpour and Nouruzi reported a polycaprolactone nanocomposite films with PVA-modified zinc oxide nanoparticles [14]. Paula and collaborators also report obtaining nanocomposites formed by *polycaprolactone* with zinc oxide nanoparticles [15]. However, the use of composites with gypsum and polycaprolactone in implants may have its performance compromised. Studies show that implants in the human body located close to regions that are submitted to radiotherapy

treatment undergo a faster degradation process [16]. Radiotherapy in cancer treatment generally occurs through doses of 1.8 to 3 Gy, reaching around 70 Gy [16]. Thus, the effects of this therapeutic dose of radiation on the implanted materials should be investigated, as it is known that the effects of radiation exposure to polymers include chain scission, cross-linking and hydrolysis. These effects depend on polymer structure, the type of radiation used, the applied dose, dose rate and irradiation conditions [16]. Several studies have been carried out on the effects of ionizing radiation in polymers and polymeric composites, however these studies have evaluated the effect of specific high doses of radiation, such as the dose of 25 kGy applied in the sterilization of biomedical artifacts [16]. Augustine and collaborators investigated the effects of gamma irradiation at doses of 15, 25, 35 and 65 kGy on the mechanical properties and cell proliferation of scaffolds formed by electrospun polycaprolactone [17]. Khan and collaborators evaluated the effects of gamma irradiation on the mechanical and barrier properties of composites formed by polycaprolactone with an irradiated carbon nanotube [18]. Paula and collaborators studied the effects of gamma irradiation at 25 kGy on the thermal and mechanical properties of nanocomposite films formed by polycaprolactone with zinc oxide nanoparticles [15]. Bruyas and colleagues investigated the effects of electron beam sterilization (25 kGy) on polycaprolactone scaffolds with β-tricalcium phosphate obtained by 3D printing [19]. Vasco et al. determined the effects of gamma irradiation (25 kGy) on sisal/polyurethane composites [20]. Wu and colleagues report the effects of high gamma irradiation on the thermal, mechanical and structural properties of composites made of glass-fiber and epoxy [21]. These various uses indicate the need for studies that analyze the effects of ionizing irradiation at therapeutic doses on polymeric materials. Few studies have evaluated the effects of ionizing radiation at a therapeutic dose on polymeric materials. Cooke and colleagues submitted polycaprolactone scaffolds immersed in an aqueous environment to therapeutic doses of radiation (50 Gy), where they observed the formation of cross-links between the polycaprolactone chains [16]. This is consistent with the work reported by Pereira-loch et al., in which the improvement in the mechanical properties of polymeric immobilizers used in radiotherapy after irradiation, therapeutic doses is attributed to the formation of cross-links between polymer chains [22].

The aim of the present investigation was to evaluate the effects of gamma irradiation at 140 Gy, as it corresponds on average to two *cancer* radiotherapy treatments, on the thermal and structural properties of composite films formed by polycaprolactone with gypsum. The films

were obtained by the solvent evaporation method and irradiated in free air at room temperature and evaluated by the experimental techniques: Infrared Spectroscopy (FT-IR), Thermogravimetric Analysis (TGA), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

2 MATERIALS AND METHODS

MATERIALS

All the reagents used were analytical grade and used as received. PCL was obtained from Sigma Aldrich (Mn 80000). Chloroform was purchased from Dinâmica. The gypsum was purchased in a market (Recife – Brazil).

PREPARATION OF PCL AND GYPSUM COMPOSITE FILMS

Gypsum particles, were added to 1 ml of chloroform and exposed to an ultrasonic bath for 30 minutes. Then the suspension with the particles and PCL were added together to solvent and kept under stirring for 24 hours. The PCL film composites, were obtained by the solvent evaporation method, using chloroform as solvent, from the slow evaporation of the solvent in air, at room temperature for 48 hours. Then the films were dried under vacuum for 48 hours. Gypsum particles were used in concentrations of 0.2%; 0.4%; 0.6%; 0.8% and 1% by mass.

IRRADIATION OF COMPOSITE FILMS

The films were exposed to gamma radiation from a ^{60}Cobalt source at 140 Gy, in the presence of air at room temperature.

INFRARED SPECTROSCOPY WITH FOURIER TRANSFORM

The absorption spectra in the infrared region by attenuated total reflectance, were obtained at room temperature in a PerkinElmer Spectrum 400 Bruker spectrophotometer FT-IR / FT-NIR. Spectra were obtained with a resolution of 4 cm^{-1}, 32 scans and a wave number between 4000 cm^{-1} and 510 cm^{-1}.

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THERMOGRAVIMETRIC ANALYSIS

The evaluation of thermal stability was determined via thermogravimetric analysis on a Shimadzu thermogravimetric analyzer, model TGA 60/60H using an alumina sample port, flow of 50 mL/min of N_2 with a heating rate of 10 ° C/min up to 600 ℃ .

X-RAY DIFFRACTION

The diffraction patterns were acquired on a Shimadzu X-ray diffractometer model XRD - 6000, Cu-Kα radiation = 1.54056 Å, with a step of 0.02 °, acquisition time of 1 second.

SCANNING ELECTRON MICROSCOPY

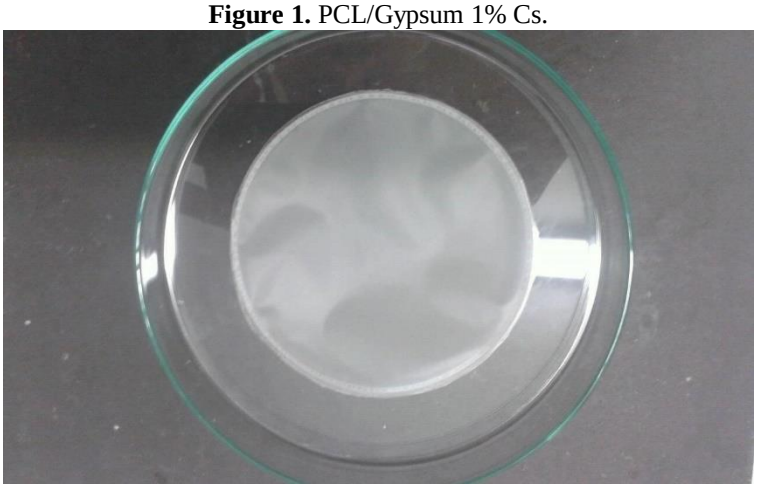
The samples were prepared on carbon tape on an aluminum support and coated with a 10–20 nm gold film, using a Bal-Tec SCD 050 sputter coater. Images were recorded by a scanning electron microscope (Tescan Mira3) operating at a voltage of 10 kV.

3 RESULTS AND DISCUSSION

PREPARATION OF PCL AND GYPSUM COMPOSITE FILMS

The films of the PCL/Gypsum Cs samples, with different mass percentages of Gypsum (0.2; 0.4; 0.6; 0.8 and 1%), were obtained by the slow evaporation of the solvent (Figure 1). The films were obtained using chloroform as solvent. They were irradiated at 140 Gy. The presentation of the chemical and structural characterization of the samples obtained follows.

Figure 1. PCL/Gypsum 1% Cs.



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FT-IR ANALYSIS OF CS

FT-IR spectroscopy was used to assess the effects of radiation at therapeutic dose and to evaluate interactions between materials. The spectra obtained for, PCL, PCL/Gypsum Cs and irradiated PCL/Gypsum Cs are shown in Figures 2 and 3. For the PCL, a peak at 1725 cm^{-1} is observed, referring to the C=O stretch of the polymer. The peaks at 2860 and 2950 cm^{-1} are attributed to the C-H bond of the polymeric chain. The PCL and PCL/Gypsum Cs exhibited practically the same spectrum. The same results were observed for samples irradiated at 140 Gy. Gao et al. observed that after the addition of 20% of calcium sulphate hemihydrate to PLLA, there was a displacement of the C = O stretch to regions of higher energy, indicating an interaction between the two components [23]. Such an effect was not seen for the evaluated Cs up to 1% gypsum.

Figure 2. FT-IR spectra of (a) PCL; (b) PCL/Gypsum 0.2%; (c) PCL/Gypsum 0.4%; (d) PCL/Gypsum 0.6%; (e) PCL/Gypsum 0.8%; (f) PCL/Gypsum 1%.

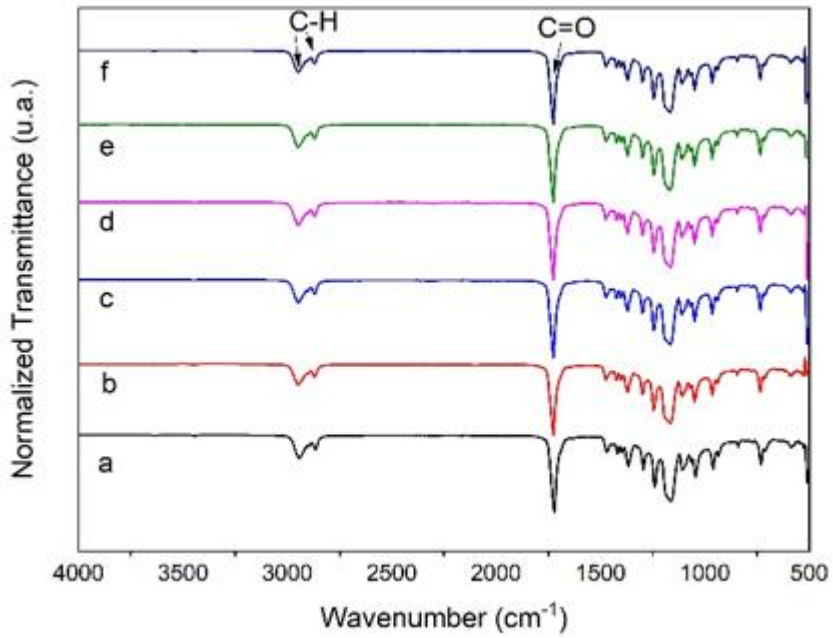

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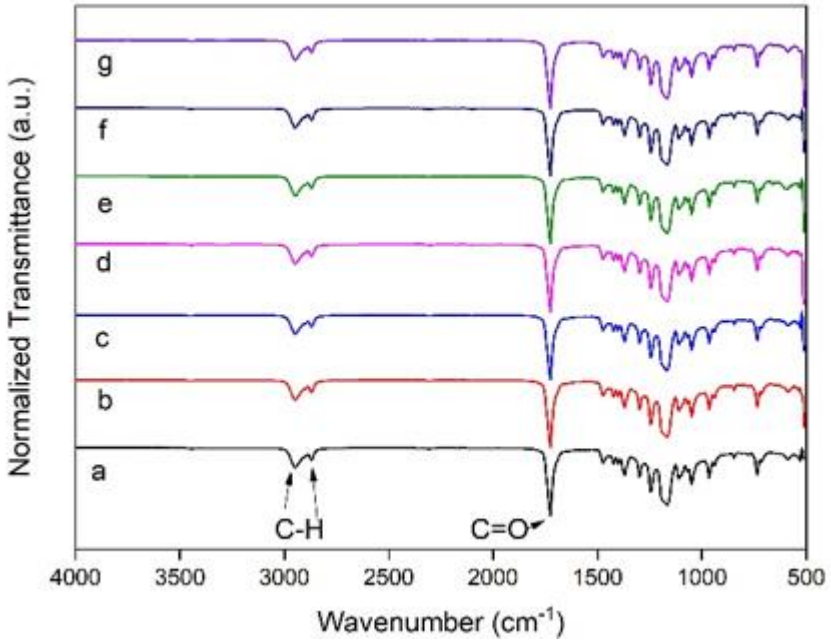
Figure 3. FT-IR spectra of (a) PCL; (b) PCL-140 Gy; (c) PCL/Gypsum 0.2%-140 Gy; (d) PCL/Gypsum 0.4%-140 Gy; (e) PCL/Gypsum 0.6%-140 Gy; (f) PCL/Gypsum 0.8% -140 Gy; (g) PCL/Gypsum 1%-140 Gy.



THERMOGRAVIMETRIC ANALYSIS

The thermal properties of PCL and PCL/Gypsum Cs were investigated by thermogravimetric analysis. Figures 4 and 5 show the mass loss curves as a function of temperature for PCL and PCL/Gypsum Cs. The PCL presented a mass loss event between 300 to 500 ˚C, which was attributed to the degradation of the polymer [14]. The TGA curves for the Cs presented a mass loss event, between 300 to 500 ˚C, attributed to polymeric degradation (Figure 4). Table 1 reports the temperatures 10% ($T_{10\%}$) and 50% ($T_{50\%}$) of decomposition of the evaluated samples.

According to what is observed in Table 1, all Cs showed values of $T_{10\%}$ and $T_{50\%}$ higher than the polymer. The addition of gypsum led to an increase in the thermal stability of the polymer. This result is attributed to the restriction of the mobility of the polymer chains, resulting from the steric impediment due to the presence of the gypsum particles [24]. The mobility restriction can be explained by the interaction established between the carbonyl group of the polymer and the calcium of the gypsum particles [23]. The irradiated samples showed the same profile of thermal degradation, with a decrease in $T_{50\%}$ for the composites analyzed, when compared to their respective non-irradiated composites (Figure 5). The decrease in $T_{50\%}$ of Cs films is attributed to formation of reactive centers, decreasing the thermal stability of the polymer [24].

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Figure 4. TGA curves of (a) PCL; (b) PCL/Gypsum 0.2%; (c) PCL/Gypsum 0.4%; (e) PCL/Gypsum 0.6%; (f) PCL/Gypsum 0.8%; (g) PCL/Gypsum 1.

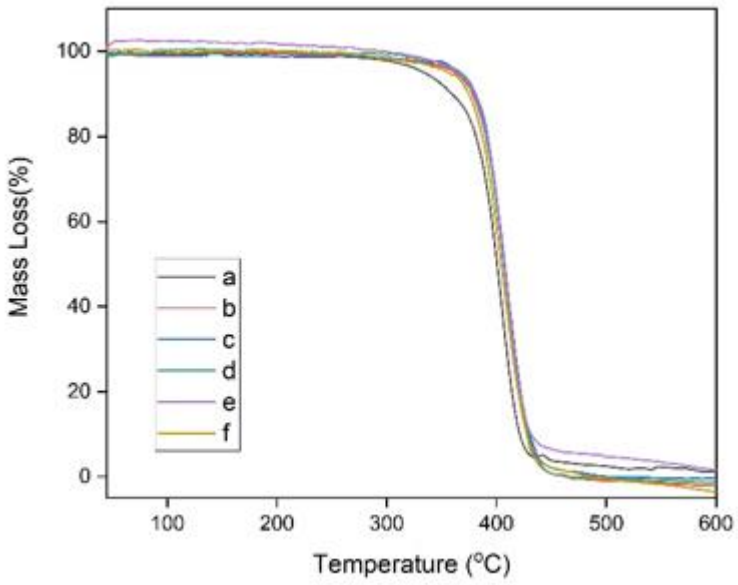

Figure 5. TGA curves of (a) PCL; (b) PCL-140Gy; (c) PCL/Gypsum 0.2% -140 Gy; (d) PCL/Gypsum 0.4% -140 Gy; (e) PCL/Gypsum 0.6%-140 Gy; (f) PCL/Gypsum 0.8% -140 Gy; (g) PCL/Gypsum 1% -140Gy.

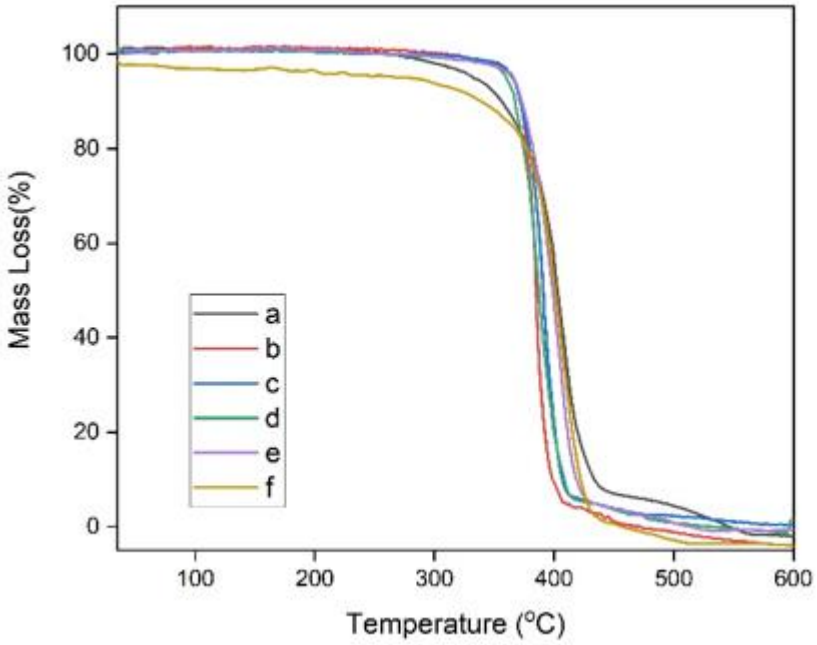

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Tabela 1. Thermal properties of PCL, PCL/Gypsum Cs and irradiated PCL/Gypsum Cs.

Sample	$T_{10\%}$(°C)	$T_{50\%}$(°C)
PCL	359	400
PCL/Gypsum 0.2%	378	407
PCL/Gypsum 0.4%	381	408
PCL/Gypsum 0.6%	380	407
PCL/Gypsum 0.8%	380	407
PCL/Gypsum 1%	374	404
PCL-140 Gy	356	403
PCL/Gypsum 0.2%-140 Gy	372	385
PCL/Gypsum 0.4%-140 Gy	372	391
PCL/Gypsum 0.6%-140 Gy	367	387
PCL/Gypsum 0.8%-140 Gy	373	399
PCL/Gypsum 1%-140 Gy	339	401

X-RAY DIFFRACTION

The diffractograms for gypsum, PCL and PCL/Gypsum Cs are shown in Figure 6. The polymer has three different reflection angles at 21.5; 22 and 23.8°, which are the planes (110), (111) and (200) of the orthorhombic crystalline structure of the polymer [25]. The gypsum diffractogram shows the characteristic crystalline behavior of the material, with peaks at 2θ = 14.67°, 25.62°, 29.76°, 31.79°, 42.28°, 49.34 °, 52.78°, 54.08°, 55.17°, associated with plans (200), (220), (400), (204), (422), (424), (207), (604) and (620) respectively [1]. The diffractograms obtained for Cs with up to 0.8% gypsum (Figure 6), did not show peaks related to gypsum, being observed only the semi-crystalline behavior of the polymer, which associated with the low content of gypsum particles caused the suppression of the gypsum diffraction phenomenon [14]. The sample with 1.0% showed peaks at 14.6° and 29.76° characteristic of gypsum, but with low intensity.

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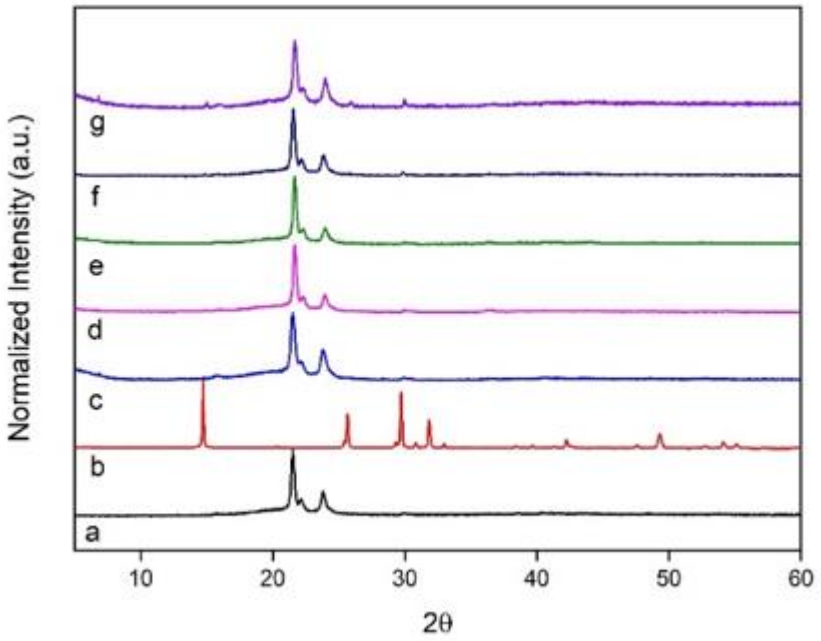
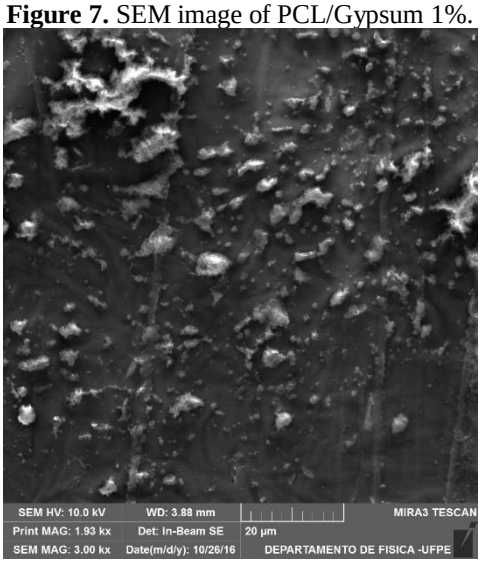
Figure 6. XRD pattern of (a) PCL; (b) PCL/Gypsum 0.2%; (c) PCL/Gypsum 0.4%; (e) PCL/Gypsum 0.6%; (f) PCL/Gypsum 0.8%; (g) PCL/Gypsum 1%.



SCANNING ELECTRON MICROSCOPY

SEM images were taken to assess the distribution of gypsum particles in the polymeric matrix. Figure 7 shows the surface morphology, referring to the PCL/Gypsum 1.0% sample, where it can be observed that the particles showed random clusters in the PCL matrix.

Figure 7. SEM image of PCL/Gypsum 1%.



4 CONCLUSIONS

Cs films with different gypsum percentages were obtained by the solvent evaporation method. The gypsum particles showed random cluster in the polymer matrix as seen in the scanning electron microscopy images. The semi-crystalline structure of the polymer was preserved after the addition of the gypsum particles. The addition of gypsum in the polymer matrix influenced the thermal properties of the polymer. Gypsum increased the thermal stability of the samples before exposure to radiation. The infrared spectra showed no distinction before and after the irradiation of Cs at 140 Gy. Few studies have been reported on the effect of a therapeutic dose of radiation on PCL and its composites with gypsum. Previous results have indicated that radiation, at therapeutic doses, alters the thermal properties of composite films.

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