WAXD and FTIR Studies of Electron Beam Irradiated Biodegradable Polymers

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Abstract. Poly(L-lactic acid) (PLLA) and poly(ε-caprolactone) (PCL) have been receiving much attention lately due to their biodegradability in human body as well as in the soil, also due to their biocompatibility, environmentally friendly characteristics and non-toxicity. Morphology of biodegradable polymers affects the rate of their biodegradation. A polymer that has high degree of crystallinity will degrade at a slower rate due to the inherent increased stability. PCL homopolymer crosslinking degree increases with increasing doses of high energy radiation. On the other hand, the irradiation of PLLA homopolymer promotes mainly chain-scissions at doses below 250 kGy. In the present work, twin screw extruded films of PLLA and PCL biodegradable homopolymers and 50:50 (w:w) blend were electron beam irradiated using electron beam accelerator Dynamitron (E = 1.5 MeV) from Radiation Dynamics, Inc. at doses in the range of 50 kGy to 10^3 kGy in order to evaluate the effect of electron beam radiation. Wide-angle X-ray diffraction (WAXD) patterns of non irradiated and irradiated samples were obtained using a diffractometer Rigaku Denki Co. Ltd., Multiflex model; and Fourier transform infrared spectroscopy (FTIR) spectra was obtained using a NICOLET 4700, attenuated total reflectance (ATR) technique. By WAXD patterns of as extruded non irradiated and irradiated PLLA it was verified broad diffusion peaks corresponding to amorphous polymer. There was a slight increase of the mean crystallite size of PCL homopolymer with increasing radiation dose. PCL crystalline index (CI) decreased with radiation dose above 500 kGy. But then, PLLA CI increased with radiation dose above 750 kGy. From another point of view, PLLA presence on the 50:50 blend did not interfere on the observed mean crystallite size increase up to 250 kGy. From 500 kGy to 10^3 kGy the crystallite size of PCL was a little bigger in the blend than the homopolymer. In contrast, FTIR results have shown that this technique was not sensitive enough to observe the degradation promoted by ionizing radiation of the studied homopolymers and blends, and neither on the miscibility of the blends.

Key words: Biodegradable polymers, PLLA, PCL, electron beam, WAXD, FTIR.

Nomenclature

PLLA:	Poly(L- lactic acid)
PCL:	Poly(ε-caprolactone)
E:	Radiation energy
WAXD:	Wide angle X ray diffraction
FTIR:	Fourier transform infrared spectroscopy

ATR:	Attenuated total reflectance
CI:	Crystalline index
A_C:	Crystalline peak area
A_T:	Total area
t:	Mean dimension of crystallites perpendicular to the (hkl) Miller planes
B:	Related to the full-width at half maximum (FWHM)
EB:	Electron beam

Greek letters

ε:	Epsilon

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1. Introduction

The problem of non-biodegradable plastic waste remains a challenge due to its negative environmental impact. In this sense, poly(L-lactic acid) (PLLA) and poly(ε-caprolactone) (PCL) have been receiving much attention lately due to their biodegradability in human body as well as in the soil, biocompatibility, environmentally friendly characteristics and non-toxicity [1-5]. PLLA: PCL blends have attracted great interest as temporary absorbable implants in human body, but they suffer from poor mechanical properties due to macro phase separation of the two immiscible components and to the poor adhesion between phases [3]. Not only chemical structure of solid polymers influences the biodegradation, but also, their highly ordered structures. Enzymatic and non enzymatic degradation occur easier in the amorphous region [6]. The controlled degradation of polymers is sometimes desired for biomedical applications and environmental purposes [7]. So, the control of the morphology of an immiscible polymer processed by melting is of vital importance for the tailoring of the final properties of the product [3].

The use of PLLA and PCL in biomedical applications requires a proper sterilization process. Nowadays, the most suitable sterilization method is high energy irradiation. Ionizing radiation exposure induces to crosslinking or scission of polymer main chain [8], besides other chemical alterations. Nature of those alterations is affected by chemical structure of polymer, and also by gaseous compounds present, as oxygen. Usually both processes take place simultaneously for many polymers. The combination of two radicals leads to crosslinking in the amorphous phase or recombination in the crystalline region, whereas chain transfer and the subsequent splitting results in chain scission [9].

Irradiation in the presence of air or oxygen leads to oxidized products formation that normally is undesirable, being less thermally stable and decreasing crosslinking degree by reaction of polymeric radicals [10].

A polymer that has high degree of crystallinity will degrade at a slower rate due to the inherent increased stability. Synthetic polymers are in general only partially crystalline, while the crystalline phase shows many defects. Many chains adopt macroconformations of helices in crystals. One of the features of semicrystalline polymers is that their lattice cell varies not only with temperature, but also systematically with crystallization conditions, annealing behaviour and plastic deformation [11, 12].

The original reasons for preparing polymer blends are to reduce costs by combining high-quality polymers with cheaper materials (although this approach is usually accompanied by a drastic worsening of the polymer properties) and to create a polymer that has a desired combination of the different properties of its components. However, according to Michler [7], usually different polymers are incompatible. Improved properties can be only realized if the blend exhibits optimum morphology. According to Sawyer [13], in polymer science, the term morphology generally refers to form and organization on a size scale above the atomic arrangement, but smaller than the size and shape of the whole sample. Thus, improving compatibility between the different polymers and optimizing the morphology are the main issues to address when producing polymer blends.

In the present work, biodegradable PLLA: PCL blend of 50:50 (w:w) and the homopolymers sheets were obtained using a twin screw extruder. The samples were irradiated with electron beam in order to evaluate the effect of the ionizing radiation on their crystalline and chemical structure. Wide-angle X-ray diffraction (WAXD) patterns of non irradiated and irradiated samples were obtained to investigate the effect on the cristallinity. Furthermore, to investigate the effects of ionizing radiation on the chemical structure of the samples, Fourier transform infrared spectroscopy (FTIR) analysis was performed.

2. Materials and Methods

Pellets of poly(ε-caprolactone), PCL, Tone[TM] P787

from Dow Chemical, and poly(L-lactic acid), PLLA, "Lacty" from Shimadzu were used for samples preparation.

2.1 Preparation of Blends and FTIR Films

PLLA was processed in a vacuum oven at 90 °C, and PCL at 40 °C overnight to eliminate the humidity in order to avoid the hydrolysis during the melt-processing. Sheets of PCL and PLLA homo-polymers and blend with PCL:PLLA weight ratio of 50:50 were prepared using a twin screw extruder (Labo Plastomill Model 150C, Toyoseki, Japan) equipped with a T-die (60 mm width and 1.05 mm thickness) of AIST, Japan. T-die temperature was set at 205 °C for PLLA homopolymer and its blends, and at 90 °C for PCL. Extruded sheets were quenched using a water bath set at room temperature. The take up speed was selected at 0.35 m·min^{-1}. As the take up speed was set at slightly higher than the extrusion out-put speed, finally obtained thickness of films was around 1 mm.

Small pieces of samples were hot pressed, in a temperature around 150 °C between two aluminium films using a small stainless steel plate and a stainless steel bar. Film thickness varied from 0.051 mm to 0.118 mm for FTIR analysis.

2.2 Electron Beam Irradiation

Samples were irradiated at IPEN-CNEN/SP, Brazil, using the electron beam accelerator Dynamitron (E = 1.5 MeV) from Radiation Dynamics Inc. Doses of 50 kGy, 100 kGy, 250 kGy, 500 kGy, 750 kGy and 10^3 kGy were applied at dose rate of 22.4 kGy·s^{-1}.

2.3 FTIR

Samples spectra of attenuated total reflectance using Fourier transform (ATR-FTIR) infrared spectroscopy were obtained at CTMSP, Brazil, using a FTIR spectrometer NICOLET 4700, with ZnSe crystal device at 45°.

2.4 WAXD

WAXD patterns of non irradiated and irradiated samples were obtained using a diffractometer Rigaku Denki Co. Ltd., Multiflex model, CuKα radiation (λ = 1.5406 Å), with tube voltage 40 kV; tube current 20 mA; step counter 0.02; counting time 4 s (first measurements) and 1 s (subsequent ones); slits DS ½°, SS ½°, KS 0.3 mm and monochromator graphite. Each diffraction pattern was normalized to make possible the samples comparison from results obtained by using different counting times.

The degree of crystallinity of the samples was calculated from X-ray patterns using the computer software to integrate total area, A_T, and crystalline peak area, A_C, to evaluate the crystalline index (CI) of the samples [14, 15], Eq. (1):

$$CI\ (\%) = \frac{A_C}{A_T} \times 100 \qquad (1)$$

## 3. Results and Discussion

3.1 WAXD Patterns

The versatility of polymeric materials, widely used in various forms, arises from the complex structural organization in these materials. X-ray diffraction has been successfully used to study various aspects of these structures in semicrystalline polymers [15]. Diffraction patterns of as extruded non irradiated and EB irradiated samples of PLLA homopolymer; PCL: PLLA (50:50) blend; and PCL homopolymer samples are shown in Figs. 1, 2 and 3, respectively.

Broz et al. [8] observed that PCL is crystalline. In Fig. 3 it is possible to observe that PCL homopolymer presents the two strongest peaks in the 2θ 21.4° and 23.7° that have been attributed in the literature to the (110) and (200) planes reflections, respectively.

In Fig. 2, it is possible to observe the two strongest reflections of PCL and a diffuse scattering due to the amorphous PLLA [16]. Non irradiated PLLA presents very small peaks intensities in the 2θ 16.4° and 18.7° in a dispersed scattering characteristic of an amorphous phase. Only for 1 MGy irradiated PLLA another peak
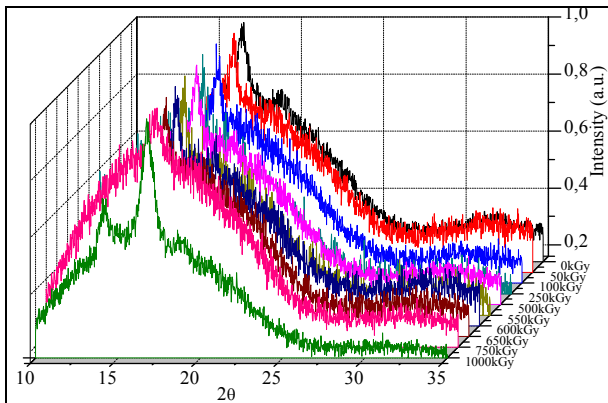
Fig. 1 PLLA irradiated with 0, 50 kGy, 100 kGy, 250 kGy, 500 kGy,550 kGy, 600 kGy, 650 kGy, 750 kGy and 10³ kGy.
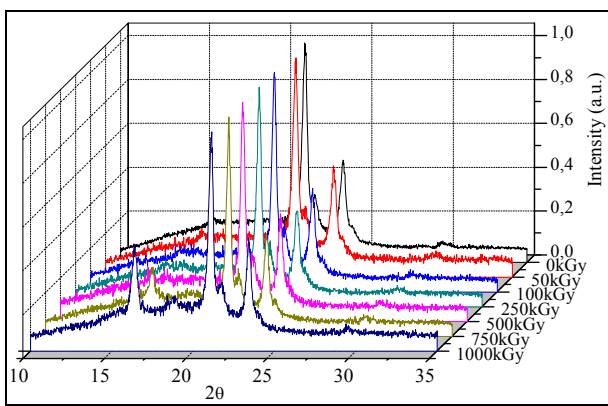
Fig. 2 PCL:PLLA 50:50 irradiated with 50 kGy, 100 kGy, 250 kGy, 500 kGy, 750 kGy and 10³ kGy.
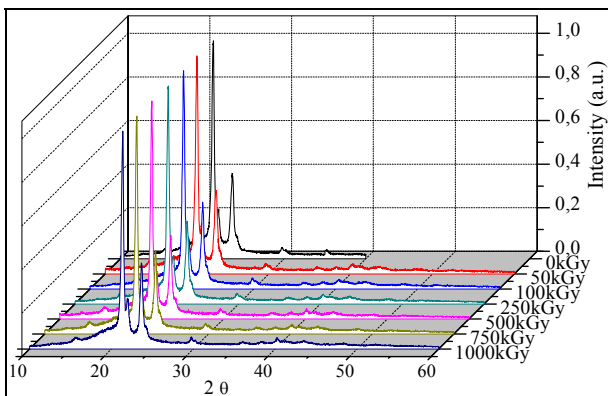
Fig. 3 PCL irradiated with 0, 50 kGy, 100 kGy, 250 kGy, 500 kGy, 750 kGy and 10³ kGy.

of small intensity appeared at 14.2°, Fig. 1.

Kantoğlu et al. [17] had cited that the crystallization of a polymer depends on the ability of the polymer molecules to align themselves to form regular ordered regions and this is achieved to a greater extent with shorter chain molecules where there are less chain entanglements. Scission in the main chain of a polymer molecule results in shorter chains being formed and hence would lead to crystallization. PLLA is a semicrystalline polymer.

3.2 Crystallinity

The crystallinity of the crystals was affected by irradiation. These random main chain scissions would occur both in the amorphous and the crystalline regions of the polymer. When PLLA was irradiated up to 80 kGy doses of gamma radiation, it underwent degradation by random main chain scission more than crosslinking, occurred equally in the amorphous and in the crystallization regions of the polymer [18]. Also, it was observed by Loo et al. [9] that the average molecular weight of PLLA drastically decreases under sample irradiation with doses up to 200 kGy. A more steady decrease was observed with increasing radiation dose indicating that chain scission is the dominant process upon electron beam irradiation [9]. It was observed in the literature that PCL crosslinking induced by ionizing radiation increases with radiation dose. On the other hand, poly(lactic acid) predominantly degrades under ionizing radiation doses below 250 kGy while crosslinking preponderates at higher doses. It was also observed that PLLA crystallinity decreased with radiation dose up to 80 kGy.

In this study, PCL samples non irradiated and EB irradiated in the range of studied radiation doses have shown the two strongest reflections at Bragg angles observed in the literature and previously mentioned. For as extruded non irradiated and irradiated PLLA samples it was observed broad diffusion peaks corresponding to amorphous polymer. An accurate examination of the broad of the X-ray profile indicates same changes related to EB irradiation into a little more crystalline.

The disorder in the crystalline domains can be evaluated by measuring the crystallite sizes which are related to the radial width $\Delta(2\theta)$ of the reflections at a scattering angle 2θ. The mean dimension of crystallites perpendicular to the (hkl) Miller planes, t, is related to

the full-width at half maximum (FWHM), B, by Scherrer's equation [9], Eq. (2):

$$t = 0.9 \frac{\lambda}{B} cos\theta \qquad (2)$$

where B is the broadening of diffraction line on the 2θ scale (radians) measured at its half maximum intensity. B is strongly affected by crystal defects and distortions, which cause line broadening [9]. There, the variation in B was used as a rough indication of the changes in crystallite size as a function of radiation dose. The half width of instrumental broadening was evaluated as 0.09° using the Si monocrystal (III). The deconvolution of the profile was done considering the profiles as cauching function. The calculated mean crystallite size for PCL and blend of PLLA: PCL as a function of EB radiation dose is presented in Table 1. The peak used for the calculation was (200) of PCL. The conditions used for crystallites sizes measurements was the same (i.e., same slit and alignment). There was a slight increase of the mean crystallite size of PCL homopolymer with increasing radiation dose. Zhu et al. [19] had observed that the crystallization of radiation crosslinked PCL was governed by heterogeneous nucleation and single-dimension growth. The crystal fraction and the crystallization rates were related to the radiation dose and degree of crosslinking. On the other hand, PLLA presence on the (50:50) blend did not interfere on the observed mean crystallite size increase up to 250 kGy. From 500 kGy to 10^3 kGy the crystallite size of PCL was a little bigger in the blend than in the homopolymer. Also it could be observed that the PCL presence on the blend affected PLLA peak increase at $2\theta = 14.2°$ on the 750 kGy and 10^3 kGy

irradiated samples, Fig. 2. Mean crystalline size of PCL homopolymer increased very slightly with radiation dose in the dose range studied. Also, PLLA presence did not affect mean crystalline size of PCL up to 100 kGy. Mean crystalline size of PCL in the blend increased a little higher than in the homopolymer of the EB irradiated above 500 kGy radiation dose, in the dose range studied.

A model that describes the semicrystalline polymers in terms of two phases, an average amorphous and an average crystalline phase, has been found to be adequate for many practical purposes. The crystalline fraction, the crystallinity or crystalline index (CI), is an important parameter in the two phase model. Crystallinity can be determined from a WAXD scan by comparing the area under the crystalline peaks with the total scattered intensity [9]. The CI values of PCL and PLLA homopolymers of non irradiated and EB irradiated samples are presented in Table 2. A_T was integrated from 10° to 35°. PCL peaks at 21.5°, 23.7° and 29.8° were used for A_C integration, Fig. 3. For PLLA it was used the peak at 16.8°for doses up to 750 kGy, and the integration of the area of the peak at 14.2° for 10^3 kGy radiation dose, Fig. 1.

Non irradiated PCL CI was 71% and decreased with radiation dose above 500 kGy. On the other hand, non irradiated PLLA CI was 12% and increased with radiation dose above 750 kGy in the studied range.

3.3 FTIR

The behaviour of polymer blends depends, in general, on the mixing degree of the components and

Table 1   Mean crystallite size (nm) for PCL and blend of PCL:PLLA 50:50 (w:w) as a function of EB radiation doses.

Sample \ Dose (kGy)	0	50	100	250	500	750	1000
PCL	19.0	18.0	18.9	21.4	20.9	21.4	21.4
PCL:PLLA	20.0	19.5	18.5	21.4	22.6	22.6	23.4

**Table 2   Crystalline index CI (%) for PCL and PLLA as a function of EB radiation doses.**

Polymer \ Dose (kGy)	0	50	100	250	500	750	1000
PCL	71	68	61	61	62	59	55
PLLA	12	10	11	9	11	16	36

their mutual interaction, as well as on the individual properties of these components. FTIR spectroscopy can be used to establish the nature and level of molecular interactions of blends. Compatibility of a blend is defined in terms of the presence of a detectable "interaction" spectrum that arises when the spectrum of the blend is compared to the spectra of the two homopolymers [8]. A technique widely used for the analysis of polymer samples with low transmission is the internal reflection spectroscopy or often called attenuated total reflectance (ATR). One problem of ATR is the inability to obtain a reproducible pressure and contact area between the sample and crystal [11]. Probably this fact occurred on the spectra (A) illustrated in Fig. 4 that shows FTIR spectrum of non irradiated PCL, PLLA homopolymers and of PLLA:PCL (50:50) blend.

If the homopolymers are compatible, an interaction spectrum with frequency shifts and intensity modifications that are intrinsic to the system will be observed. If the homopolymers are incompatibles, the spectrum of the blend is simply the spectral sum of the spectra of the two polymers, within experimental error [20]. In the case of PLLA: PCL blend, both components are hydroxy acid polymers, having the same functional groups, as showed in Fig. 4 and Fig. 5. The difference between them is the higher amount of CH_2 groups on PCL structure that shows more peaks of absorption at 750-1,500 cm^{-1} region. Although, there is no absorption band frequency shifts but only intensity modifications, PLLA and PCL seems to be a compatible blend and in fact they are immiscible [3].

The irradiation of polymeric materials with ionizing radiation, as gamma rays or accelerated electrons, leads to the formation of very reactive intermediate species including free radicals, ions and excited states.

These intermediates can follow several reaction paths, which can result in disproportion, hydrogen abstraction, arrangements and/or the formation of new bonds [21].
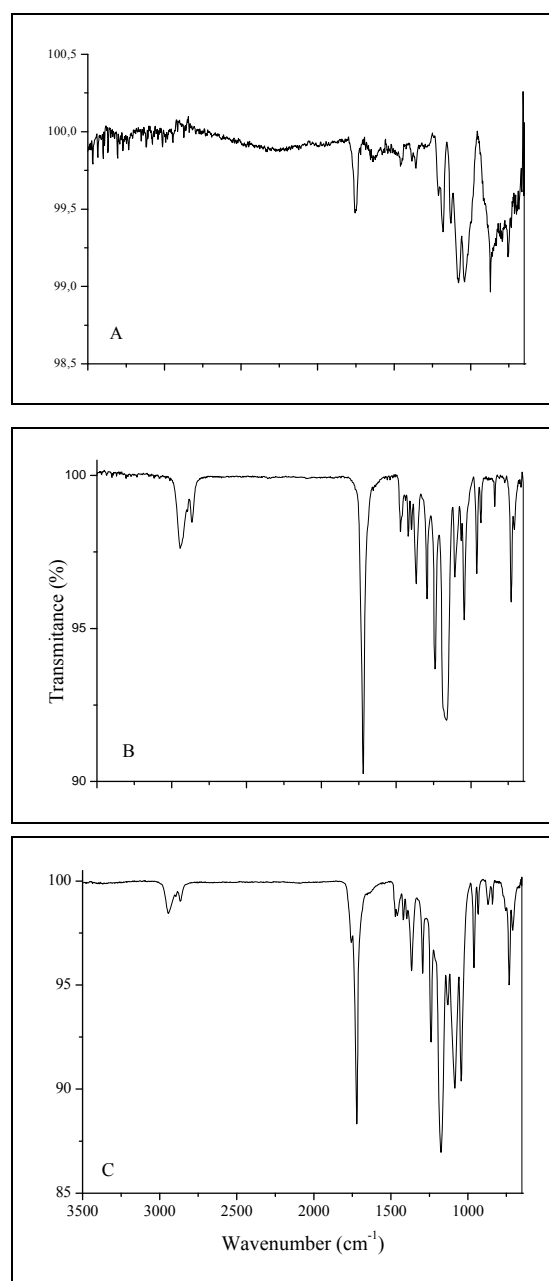
Fig. 4   FTIR-ATR spectrum of non irradiated A) PLLA, B) PCL, and C) PCL:PLLA (50:50) blend.

As a result of the radiation effect, the polymers are subject in varying extents to degradation and crosslinking reactions. Parameters such as morphology, chemical structure of the polymer, dose and irradiation media determine whether crosslinking or chain scission is the dominating effect of the irradiation process [8]. In addition to crosslinking and/or scission, other
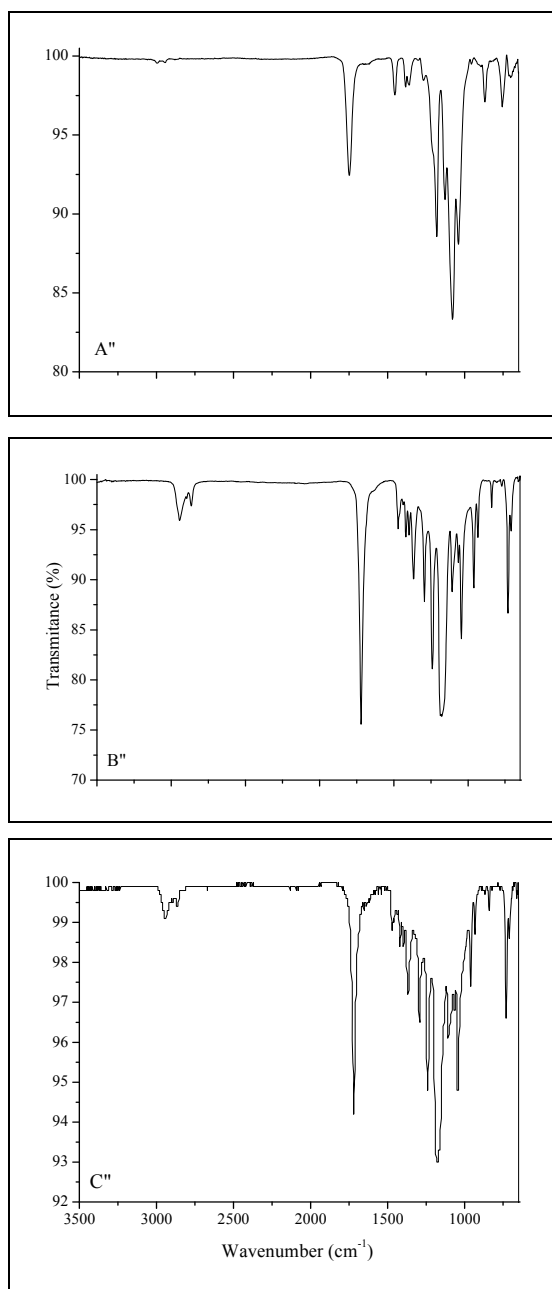
**Fig. 5   FTIR-ATR spectrum of EB irradiated samples of A")
PLLA, B") PCL, and C") PCL:PLLA (50:50) blend.**

chemical changes can occur depending on the chemical structure of the polymer, and also gases generation such as oxygen. Irradiation in the presence of air or oxygen leads to oxidized products, which are often undesirable, being thermally less stable and also detracting from the degree of crosslinking by reacting with polymer radicals [19].

Although it would be expected to observe some

modification on functional groups of the irradiated PCL and PLLA homopolymers and blends by FTIR, it is very difficult to detect minor chemical changes occurring on the polymer chain. That can be due to the fact that infrared bands of polymers are inherently broad and weak. It would be necessary to eliminate from the observed spectrum the interfering absorptions of the unreacted functional groups present in the polymer. This elimination step could be accomplished by using absorbance subtraction of the control polymer spectrum from the reacted system, obtaining a resulting spectrum with the chemical reactions that have occurred [20]. The reason may be that it is difficult to obtain reproducible spectra by FTIR-ATR. In this study it was not possible to subtract the PLLA and PCL homopolymers from PLLA:PCL blend in order to observe the modification induced by the ionizing radiation. With the aim of evaluate the effect of dose on the homopolymers and blend, samples were irradiated by electron beam and the FTIR-ATR spectra obtained are shown in Fig. 5. FTIR was not sensitive enough to observe polymer degradation induced by EB irradiation, neither, to observe the influence on the miscibility of the polymer blends by the irradiation. As the organization of the polymeric structure affects the biodegradability, in the literature FTIR was used to evaluate possible changes in the PLLA crystallinity [5]. Although, it has been observed that a new band appeared in the C=O stretching band region from 1,810 to 1,710 cm^{-1}, in this case it was not possible to observe it, neither the 955 cm^{-1} band ascribed as an amorphous band and the 921 cm^{-1} band attributed to 10_3 helix associated to the crystalline form [5].

4. Conclusions

FTIR-ATR has not shown enough sensibility to demonstrate polymer degradation in significant extent in EB irradiated samples. Although no spectral band frequency shifts were observed but only intensity modifications, PLLA: PCL seems to be an immiscible blend. PCL samples, non irradiated and irradiated

samples, show the two strongest reflections at Bragg angles that have been attributed in the literature to the (110) and (200) reflections planes. For PLLA samples as extruded non irradiated and irradiated with all studied doses it was observed broad diffusion peaks corresponding to amorphous polymer and very small crystalline peaks. From 500 kGy to 10^3 kGy the crystallite size of PCL is a little bigger in the blend than the homopolymer. Also it can be observed that the PLLA peak increase at $2\theta = 14.2°$ is affected by PCL presence on the blend. PCL crystalline index (CI) decreases with radiation dose. On the other hand, PLLA CI increases with radiation dose above 750 kGy.

Acknowledgments

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