

# Investigation of irradiated biodegradable blends by FTIR and wide-angle X-ray diffraction

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**Abstract.** In the present work, twin screw extruded films of PLLA and PCL biodegradable homopolymers and 50:50 (w:w) blend were irradiated with gamma rays from Co-60 and electron beam at doses in the range of 50 to 500 kGy in order to evaluate the effect of irradiations on homopolymers and blend. The FTIR results have shown that this technique was neither sensitive enough to observe the degradation promoted by ionizing radiation of studied homopolymers and blends and, nor on the miscibility of the blends. Wide-angle X-ray diffraction (WAXD) of PCL samples, non-irradiated and irradiated showed two strongest reflections at angles  $2\theta = 21.4^\circ$  and  $2\theta = 23.7^\circ$  that have been attributed in the literature to the (110) and (200) reflections, respectively. As for extruded non-irradiated and irradiated PLLA, it was observed broad diffusion peaks corresponding to an amorphous polymer. PLLA annealed samples showed reflections at angles  $2\theta = 16.4^\circ$  and  $2\theta = 18.7^\circ$  previously attributed in the literature to distorted  $10_3$  ( $\alpha$ -form) helices. It was possible to observe slight alteration of the crystallite size of all irradiated samples of PCL in the dose range studied.

**Key words:** WAXD • FTIR • PLLA • PCL • ionizing radiation

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Received: 27 October 2008  
Accepted: 20 May 2009

## Introduction

The non-biodegradable plastic waste has become crucial in recent years especially concerning environmental impact. Poly(L-lactic acid) (PLLA) and poly( $\epsilon$ -caprolactone) (PCL) have been receiving much attention lately due to their biodegradability in human body as well as in soil, biocompatibility, environmentally friendly characteristic and non-toxicity [6, 8, 20, 21, 26–28]. PLLA is a poly( $\alpha$ -hydroxy acid) and PCL is a poly( $\omega$ -hydroxy acid) [21]. PLLA is a hard, transparent and crystalline polymer [23]. On the other hand, PCL can be used as a polymeric plasticizer because of its ability to lower elastic modulus and to soft other polymers [8].

To improve some desirable properties and for economical reasons, two or more polymers can be mixed to form polymeric blends [15]. PLLA:PCL blends have attracted great interest as temporary absorbable implants in human body, but they suffer from poor mechanical properties due to macrophase separation of the two immiscible components and to the poor adhesion between phases [6]. Not only the chemical structure of solid

\* Presented on the International Conference on Recent Developments and Applications of Nuclear Technologies, 15-17 September 2008, Białowieża, Poland.

polymers influences the biodegradation, but also their highly ordered structures. Enzymatic and non enzymatic degradation occur more by ease in the amorphous region [3, 12, 14, 15, 19, 22, 23, 25]. The morphology of the blends affects the thermomechanical properties [17] as well as the biodegradation of the polymers. So, the control of the morphology of an immiscible polymer processed by melting is of vital importance for tailoring of the final properties of the product [6].

PLLA is hydrolytically unstable, and for both PLLA and PCL to be used in biomedical applications it is necessary a proper sterilization, the most suitable sterilization method is high energy irradiation. However, polymeric structural changes such as scission and cross-linking is induced by radiation processing of polymers [10]. Usually both these 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 [13].

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, whereas the crystalline phase shows many defects [1].

Many chains adopt macroconformations of helices in crystals [7]. 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 [1].

In view of the fact that was explained previously, it is important to investigate the effect of ionizing radiation on polymers. So, in the present work, biodegradable PLLA:PCL blends of various compositions were obtained using a twin screw extruder. They were irradiated with gamma rays from Co-60 and electron beam radiation in order to evaluate the effect of ionizing radiation on the chemical structure of samples by FTIR. Wide-angle X-ray diffraction (WAXD) patterns of non-irradiated and irradiated samples were obtained to investigate the effects of ionizing radiation on the crystalline structure.

## Materials and methods

### 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 hydrolysis during the extrusion process. Blends were prepared using a twin screw extruder Labo Plastomill Model 50C 150 from Toyoseki, at Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Japan. The homopolymers PCL and PLLA and blends with PCL:PLLA weight ratios of 25:75, 50:50 and 75:25 were extruded at 10 rpm. The sheets were obtained from a horizontal *T*-die (60 × 1.05 mm). Water bath at room temperature was used to cool the sheets after extrusion, whose surface level was at a 5 m distance of 55 mm from the *T*-die. The take up speed was 0.35 m·min<sup>-1</sup>.

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

### Gamma and electron beam irradiation

Samples were irradiated at IPEN-CNEN/SP, Brazil, using a Co-60 irradiator, Gammacell model 220, series 142 from the Atomic Energy of Canada Limited. Doses of 50, 100, 150, 200 and 500 kGy were applied at a dose rate of 1.2 Gy·s<sup>-1</sup>.

Samples were irradiated at IPEN-CNEN/SP, Brazil, using an electron beam accelerator Dynamitron (*E* = 1.5 MeV) from Radiation Dynamics, Inc. Doses of 50, 100, 250 and 500 kGy were applied at a dose rate of 22.4 kGy·s<sup>-1</sup>.

## Methods

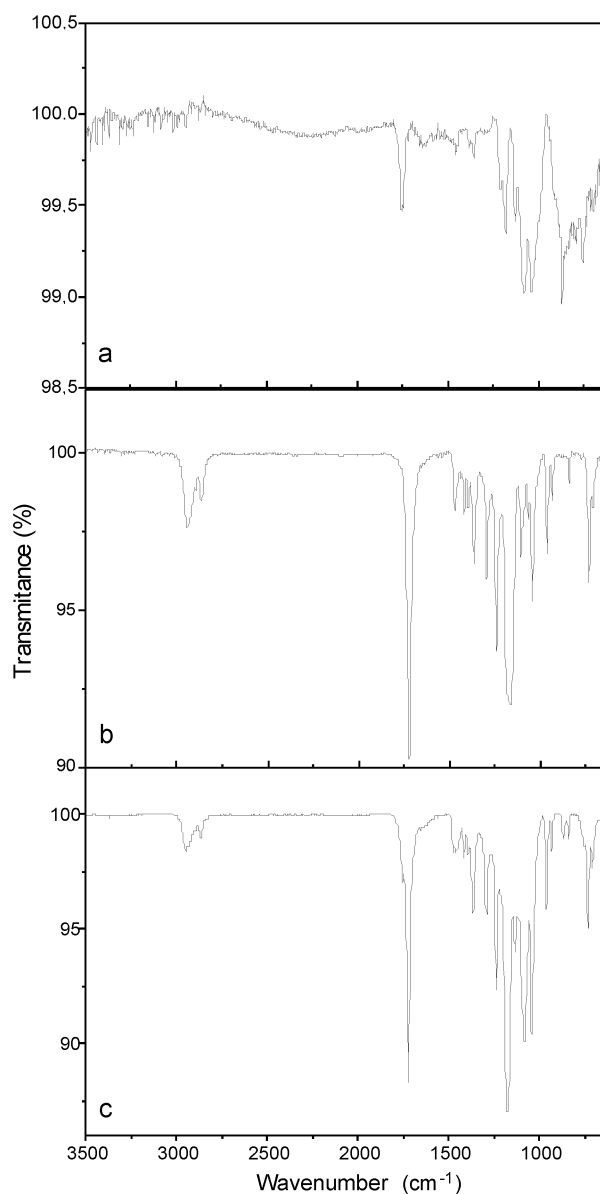
FTIR samples spectra were obtained at CTMSP-SP, Brazil, using a FTIR spectrophotometer NICOLET 4700, by ATR technique with a ZnSe crystal device at 45°.

WAXD patterns of non-irradiated and irradiated samples with 100 and 500 kGy were obtained using a diffractometer Rigaku Denki Co. Ltd., Multiflex model, CuK<sub>α</sub> radiation ( $\lambda = 1.5406 \text{ \AA}$ ). 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; monochromator graphite. Each diffraction pattern was normalized to make it possible the samples comparison from results obtained by using different counting times.

## Results and discussion

FTIR spectroscopy can be used to establish the nature and level of molecular interactions of blends. The behaviour of polymer blends depends, in general, on the mixing degree of the components and their mutual interaction, as well on the individual properties of these components. From an IR point of view, 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 [18]. 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 [1]. Probably this fact occurred on the spectra (a) showed in Fig. 1 that shows FTIR spectrum of non-irradiated PCL, PLLA homopolymers and of PLLA:PCL 50:50 (w:w) blend.

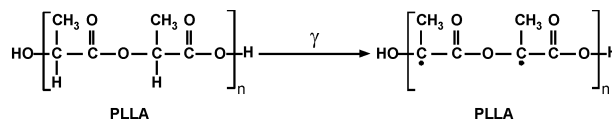
If the homopolymers are compatible, an interaction spectrum with frequency shifts and intensity modifications that are intrinsic to the system will be observed. If the homopolymers are incompatible, the spectrum of the blend is simply the spectral sum, within experimental error, of the spectra of the two polymers [11]. In the



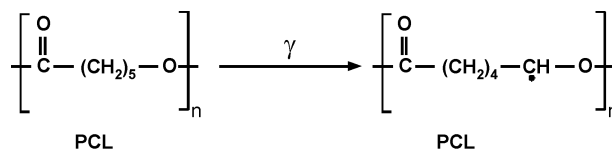
**Fig. 1.** FTIR spectrum of: a – PLLA; b – PCL homopolymers; c – PCL:PLLA 50:50 blend, non-irradiated.

case of PLLA:PCL blend, both components are hydroxy acid polymers, having the same functional groups, as showed in Figs. 2 and 3. The difference between them is the higher amount of  $\text{CH}_2$  groups on PCL structure that shows more peaks of absorption in the 750–1500  $\text{cm}^{-1}$  region. Although, there is no absorption band frequency shifts, only intensity modifications, PLLA and PCL seems to be a compatible blend and, in fact, they are immiscible [6].

The irradiation of polymeric materials with ionizing radiation, such 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 [17]. The possible radical formed for  $\gamma$ -irradiated PLLA is shown in Fig. 2, according to the literature [10]. Furthermore, the probable radical formed in EB irradiated PCL samples is shown in Fig. 3 [18].



**Fig. 2.** Possible radical species formed in PLLA irradiated samples [10].

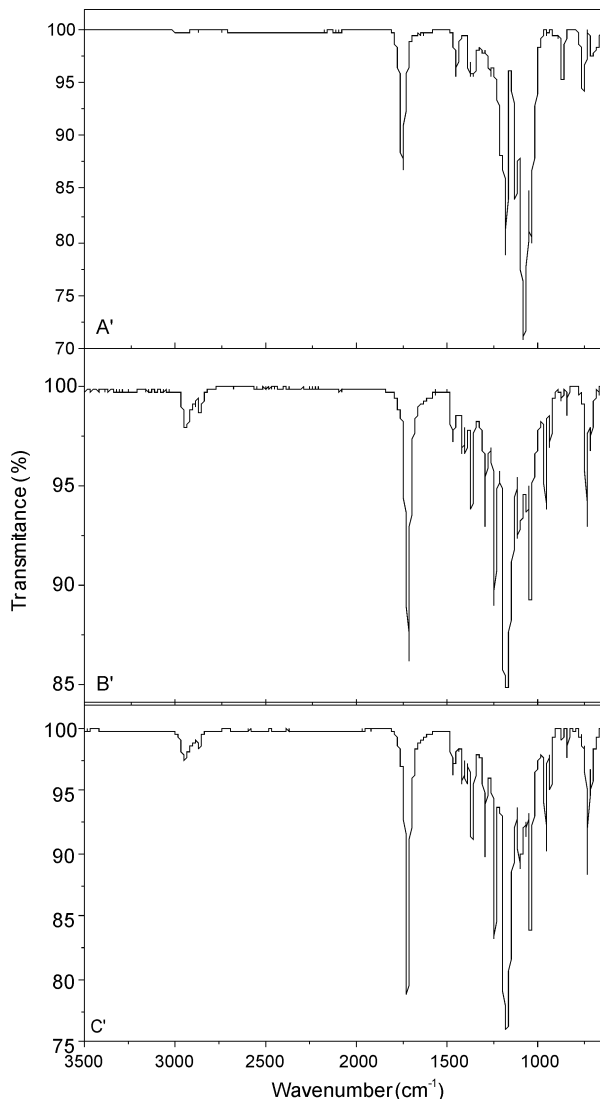


**Fig. 3.** Probable radical species formed in PCL irradiated samples [18].

As a result of the radiation effect, the polymers are the 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 [18]. In addition to crosslinking and/or scission, other 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 [4].

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 IR 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 spectrum of the control polymer from the reacted system, obtaining a resulting spectra with the chemical reactions that have occurred [11]. Maybe because it is difficult to obtain reproducible spectra by ATR technique, 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 ionizing radiation. In order to evaluate the effect of dose rate on the homopolymers and blend, samples were irradiated by gamma rays and electron beam and, the FTIR spectrum obtained are shown in Figs. 4 and 5, respectively. For this study, it was chosen the highest similar doses of both gamma and EB radiation.

A significant difference exists between electron beam and gamma processing of polymers, which is related to dose rate and often to oxidative degradation of material at or near the surface for reactions conducted at low-dose rates [5]. FTIR was neither sensitive enough to detect polymer degradation in significant extent due to both gamma and EB radiation, nor on the miscibility of the polymer blends by the irradiation. Also here, it was not possible to evaluate by FTIR the influence of the dose rate on the irradiated polymers without making any spectrum treatment.



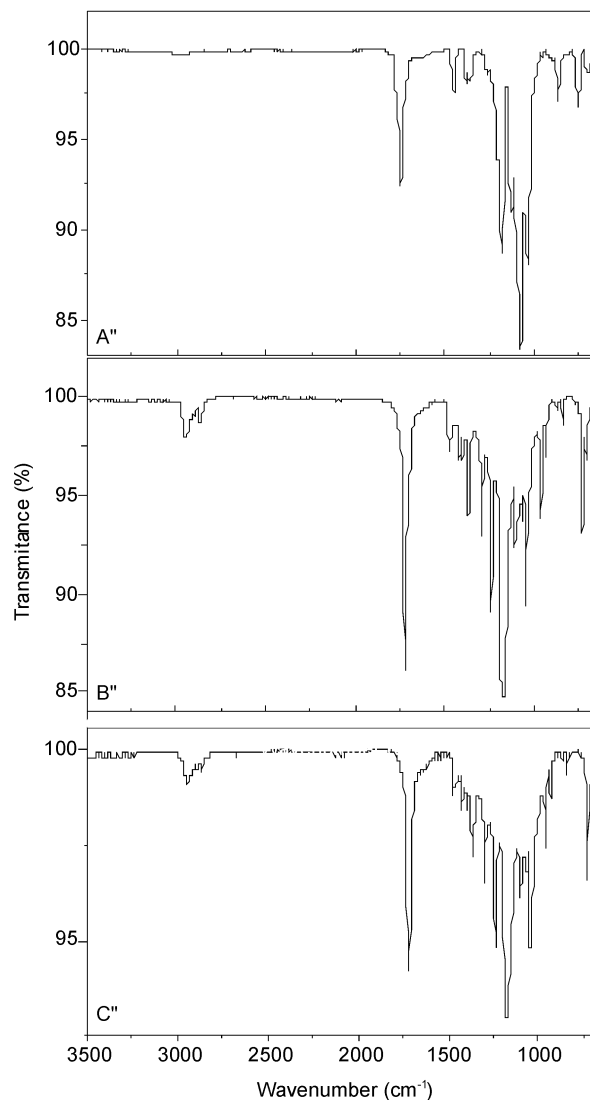
**Fig. 4.** FTIR spectrum of A' – PLLA; B' – PCL homopolymers; C' – PCL:PLLA 50:50 blend, gamma irradiated.

As the organization of the polymeric structure affects the biodegradability, in the literature FTIR was used to evaluate possible changes in the PLLA crystallinity [28]. Although, it had been observed that a new band appeared in the C=O stretching band region 1810–1710 cm<sup>-1</sup>, in this case it was neither possible to observe it, nor the 955 cm<sup>-1</sup> band ascribed to an amorphous band and the 921 cm<sup>-1</sup> band to 10<sub>3</sub> helix associated to the crystalline form.

Diffraction patterns of non-irradiated; gamma and EB irradiated with 100 and 500 kGy PLLA homopolymer; PCL:PLLA 50:50 blend; PCL homopolymer as extruded samples are shown in Figs. 6, 7 and 8, respectively. All patterns of irradiated samples were dislocated in both axis to better visualization. PLLA annealed homopolymer is shown in Fig. 9.

Broz *et al.* observed that PCL is crystalline [2]. In this work, in Fig. 7 it is possible to observe that the PCL homopolymer presents strongest peaks at  $2\theta$  21.4° and 23.7° that have been attributed in the literature to the (110) and (200) reflections, respectively.

In Fig. 6, it is possible to observe the two strongest reflections of PCL and a diffuse scattering due to the amorphous PLLA [24]. Non-irradiated PLLA presents

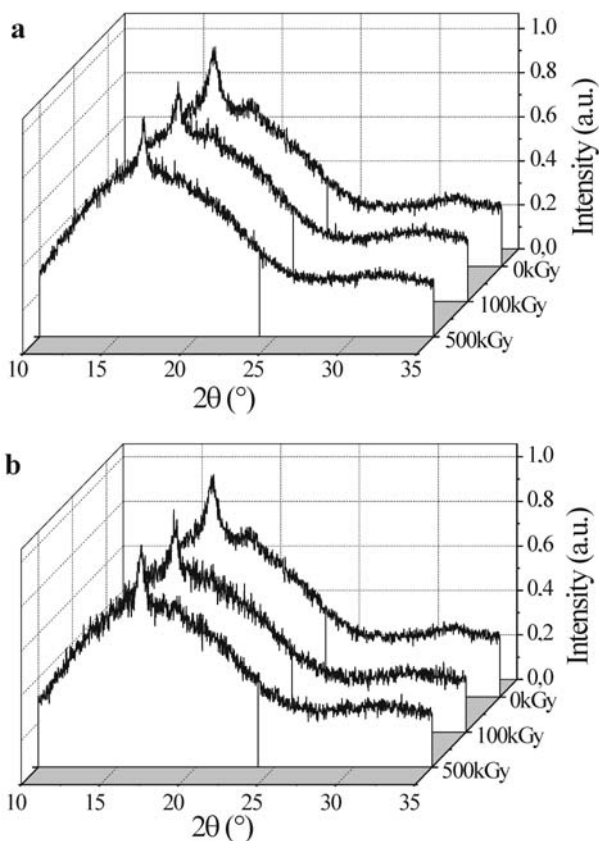


**Fig. 5.** FTIR spectrum of A'' – PLLA; B'' – PCL homopolymers; C'' – PCL:PLLA 50:50 blend, EB irradiated.

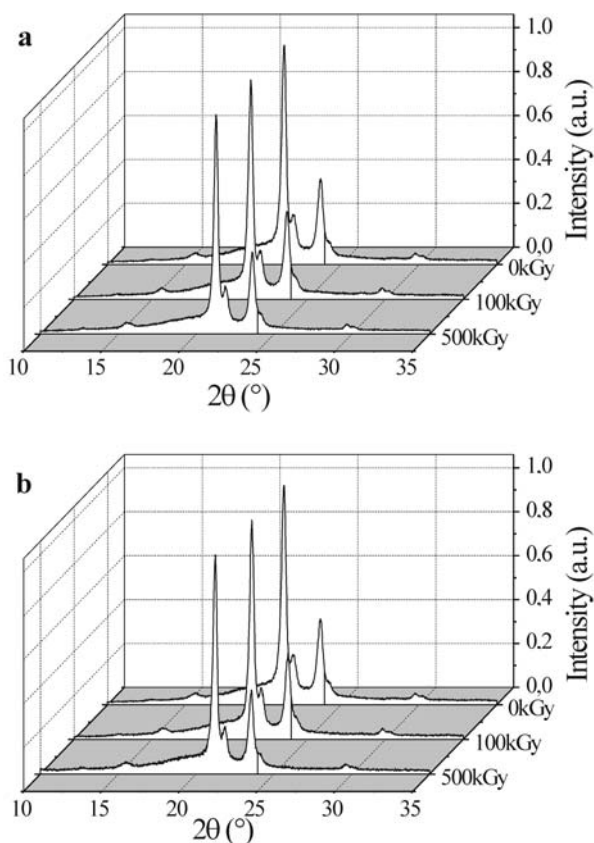
very small peak intensities at  $2\theta$  16.4° and 18.7° in a dispersed scattering characteristic of an amorphous phase (Fig. 8). When PLLA is annealed, Fig. 9, it is possible to observe two strong peaks intensities at angles =  $2\theta$  16.4° and 18.7° and a small peak at 22.5°. PLLA as extruded sample is amorphous and crystallizes by thermal treatment.

By annealing the semi-crystalline polymers in appropriate conditions, the thermal history due to processing can be eliminated and also permits the crystallization to occur. Zhang *et al.* [28] studied two different annealing temperatures of PLLA powder samples, 80 and 140°C, and observed the strongest peaks at  $2\theta$  = 16.7° and 19.1° and a small peak at  $2\theta$  = 22.3° for the annealed PLLA powder samples at 140°C indicating the appearance of phase  $\alpha'$ . The same peaks was observed in this work for PLLA sheet annealed at the same temperature, the strongest peaks at  $2\theta$  = 16.4° and 18.7° attributed to the (200) and (203) planes and a small peak at 22.5° (indicated by an arrow in the upper figure in Fig. 9) characteristic of phase  $\alpha'$  that is not observed for the 80°C annealed sample.

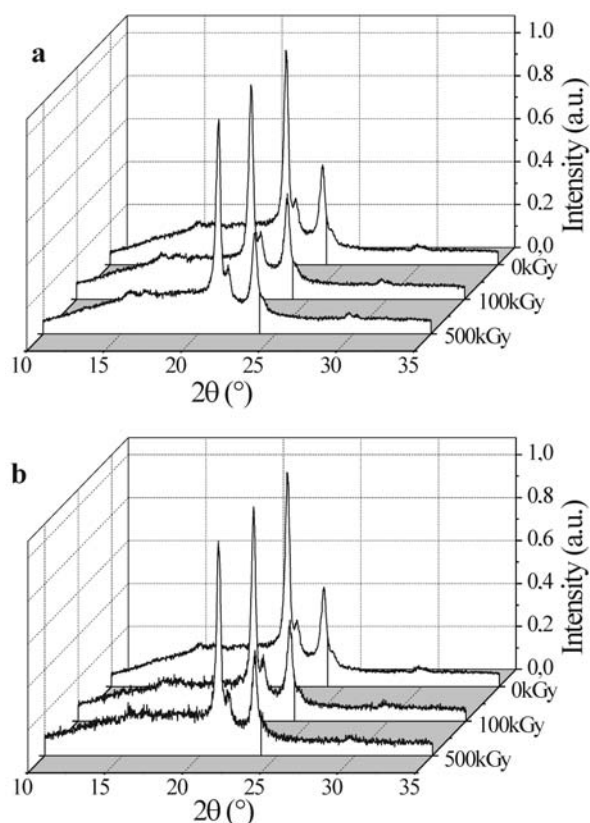
Due to the fact that it was possible to observe only a slight alteration on the crystallite size of PCL on the 100 kGy irradiated samples, further, it was analyzed the



**Fig. 6.** WAXD patterns of extruded PLLA non-irradiated, a – gamma; b – EB irradiated with 100 and 500 kGy.



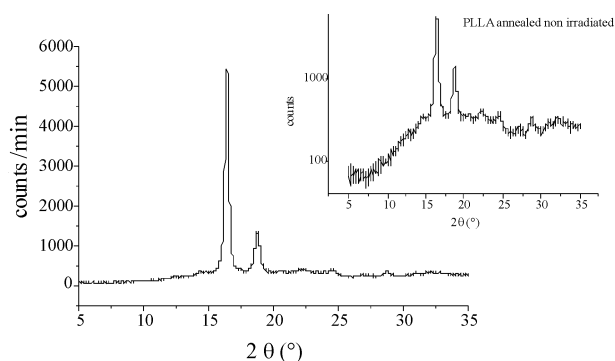
**Fig. 7.** WAXD patterns of extruded PCL non-irradiated, a – gamma; b – EB irradiated with 100 and 500 kGy.



**Fig. 8.** WAXD patterns of extruded PCL:PLLA 50:50 (w:w) non-irradiated, a – gamma; b – EB irradiated with 100 and 500 kGy.

500 kGy irradiated sample and the smaller doses were not analyzed in this study.

Kantoglu *et al.* [9] 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. The crystallinity of the formed crystals had been 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 [9]. Also, it was



**Fig. 9.** WAXD pattern of PLLA annealed, non-irradiated (the upper figure Y axis changed to the logarithm scale).

observed by Loo *et al.* [13] that the average molecular weight of PLLA drastically decreases up to 200 kGy. And a more steady decrease was observed with increasing radiation dose, indicating that chain scission is the dominant process upon electron beam irradiation [13]. 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 at ionizing radiation doses below 250 kGy and crosslinking preponderates at higher doses. It was also observed that PLLA crystallinity decreases with radiation dose up to 80 kGy.

In this work, PCL samples, non-irradiated and gamma irradiated with 100 and 500 kGy radiation doses, show the two strongest reflections at Bragg angles observed in the literature and mentioned previously here. For extruded non-irradiated and irradiated with 100 and 500 kGy doses PLLA samples, it was observed broad diffusion peaks corresponding to amorphous polymer. PLLA samples annealed under temperature of 140°C during half an hour, showed reflections at Bragg angles as described previously in the literature that are attributed to 10<sub>3</sub> ( $\alpha'$ -form) distorted helices. An accurate examination of the broad of the X-ray profile indicates same changes related to gamma 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 widths  $\Delta(2\theta)$  of the reflections at a scattering angle  $2\theta$  by the Scherrer equation, (Eq. (1)).

In reality, there are two contributions to the width: one is the size and the other is the paracrystallinity or microstrain [16].

The mean dimension of crystallites perpendicular to the *hkl* planes,  $t$ , is related to the full-width at half maximum (FWHM),  $B$ , by Scherrer's equation [13]:

$$t = 0.9\lambda / B \cos\theta$$

where  $B$  is the broadening of diffraction line on the  $2\theta$  scale (radians) measured at its half maximum intensity. The  $B$  is strongly affected by crystal defects and distortions, which cause line broadening [13]. There, the variation in the  $B$  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. Table 1 shows the calculated mean crystallite size for PCL and blend of PLLA:PCL. The peak used for the calculation was

**Table 1.** Mean crystallite size for PCL and blend of PCL:PLLA 50:50 (w:w) gamma irradiated

Sample	Non-irradiated	100 kGy	500 kGy
PCL	20.7 nm	21.5 nm	24.0 nm
PCL/PLLA	19.5 nm	20.9 nm	24.7 nm

**Table 2.** Mean crystallite size for PCL and blend of PCL:PLLA 50:50 (w:w) EB irradiated

Sample	Non-irradiated	50 kGy	100 kGy	250 kGy	500 kGy
PCL	19.0 nm	18.0 nm	18.9 nm	21.4 nm	20.9 nm
PCL/PLLA	20.0 nm	19.5 nm	18.5 nm	21.4 nm	22.6 nm

(200) of PCL. The conditions used for crystallites sizes measurements was the same (i.e. same slit and alignment).

There is a small increase of the mean crystallite size with increasing radiation dose. Zhu *et al.* [29] had observed that the crystallization of radiation cross-linked PCL was governed by heterogeneous nucleation and single-dimension growth; the crystal fraction and rates of crystallization were related to the radiation dose and degree of crosslinking. On the other hand, PLLA presence on the 50:50 blend do not interfere with the observed mean crystallite size increase.

Comparing gamma irradiated to electron beam irradiated samples (Figs. 6–8) it was not possible to observe by WAXD the influence of dose rate. It is possible to observe for EB irradiated samples the same peaks observed for gamma irradiated samples. Also here, it is possible to observe that PLLA is amorphous and the EB radiation does not affect this property.

Table 2 shows the calculated mean crystallite size for PCL and blend of PLLA:PCL EB irradiated with radiation doses of 50, 100, 250 and 500 kGy. The peak used for the calculation was (200) of PCL.

Mean crystalline size of PCL homopolymer increase with radiation dose is lower than gamma irradiated samples in the dose range studied. Also, PLLA presence does not affect mean crystalline size of PCL. Mean crystalline size of PCL in the blend increases a little higher than the homopolymer, to the EB irradiated with 500 kGy radiation dose.

## Conclusion

In this case FTIR was not sensitive enough to observe polymer degradation to an significant extent in both gamma and EB irradiated samples, even though the effects of ionizing radiation on polymers are well known. Also, it was not possible to evaluate by FTIR the influence of the dose rate on the irradiated polymers, some spectrum treatment is required. Although no spectral band frequency shifts were observed, only intensity modifications, PLLA:PCL is a immiscible blend. Also, it was not possible to observe by FTIR the effect of radiation dose on the miscibility of the polymer blends. PCL samples, non-irradiated and irradiated with 100 and 500 kGy radiation doses, show the two strongest reflections at angles  $2\theta = 21.4^\circ$  and  $2\theta = 23.7^\circ$  that have been attributed in the literature to the (110) and (200) reflections, respectively. As for extruded non-irradiated and irradiated with 100 and 500 kGy doses PLLA samples, it was observed broad diffusion peaks corresponding to amorphous polymer. PLLA samples annealed under a temperature of 140°C during half an hour, showed reflections at angles  $2\theta = 16.4^\circ$  and  $2\theta = 18.7^\circ$  previously attributed in the literature to distorted 10<sub>3</sub> ( $\alpha'$ -form) helices. PLLA, as extruded samples, are amorphous and crystallize by thermal treatment. It was possible to

observe slight alteration of the crystallite size of PCL in all irradiated blends in the dose range studied.

**Acknowledgment.** Polymer extrusion was performed in Tsukuba, Ibaraki, Japan and WAXD patterns were obtained in São Paulo, São Paulo, Brazil.

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