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INVESTIGATION OF GAMMA IRRADIATED PCL/PLLA BLEND BY WIDE-ANGLE X- RAY DIFFRACTION

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ABSTRACT

Biodegradable polymers are able to undergo deleterious changes in their properties due to an alteration in the chemical structure mediated at least partially by a biological system. It was observed in the literature that crosslinking of poly(ε-caprolactone), PCL, increases with the radiation dose induced by ionizing radiation. 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 Poly(L-lactic acid), PLLA crystallinity decreases with radiation dose up to 80 kGy. In the present work, twin screw extruded films of PLLA and PCL homopolymers and 50/50 (w/w) blend were irradiated with gamma rays from Co-60 at doses in the range of 25 to 500 kGy to investigate the effects of the ionizing radiation on their crystalline structure by wide-angle X- ray diffraction (WAXD). PCL samples, non irradiated and irradiated with 100 and 500 kGy, showed the two strongest reflections at Bragg angles 2θ =21.4° and 2θ =23.7° that have been attributed in the literature to the (110) and (200) reflections, respectively. For as extruded non irradiated and irradiated with 100 and 500 kGy doses PLLA it was observed broad diffusion peaks corresponding to amorphous polymer. PLLA annealed samples showed reflections at Bragg angles 2θ =16.4° and 2θ =18.7 ° previously attributed in the literature to distorted 10_3 (α-form) helices. It was possible to observe slight alteration on the crystallite size of all irradiated samples of PCL in the dose range studied.

1. INTRODUCTION

Poly(L-lactic acid), PLLA, and poly(ε-caprolactone), PCL, have been receiving much attention due to their biocompatibility, non toxicity and biodegradability in human body as well as in the soil [1-7]. Biodegradable polymers are able to undergo deleterious changes in their properties due to an alteration in the chemical structure mediated at least partially by a biological system. Chemical structure influences the biodegradation of solid polymers. Enzymatic and non enzymatic degradations occur easier in the amorphous region [8, 9-14]. The morphology of the blends affects the thermomechanical properties [15] as well as the biodegradation of the polymers. So the control of the morphology of an immiscible polymer blend processed by melting is important for the tailoring of the final properties of the product [3]. 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 moreover the crystalline phase shows many defects [16].

Radiation has been known to alter the physical properties of polymers through main-chain scission and crosslinking. 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 [17].

Many chains adopt macroconformations of helices in crystals. A helix is characterized by the symbol *aA*B/N*, where *a*=type of repetition along the longitudinal axis, *A*=helix class (=number of skeletal chain atoms contained within the helix residue; the motif), *B*=integral number of conformation repeating unit per *N* turns, *N*= number of turns needed to return to the original position, and *,/=separators. Repetitions may be translations *t* or screw repetitions *s*. *a* and/or *A* are often omitted and the helix structure is simply described by B_N [18]. One of the features of semicrystalline polymers is that their lattice cell varies not only with temperature, but also systematically with crystallization conditions, annealing behavior and plastic deformation [16]. In the literature [7] three crystalline modifications (α, β,γ) of PLLA have been identified upon changing the preparation conditions. The α form is believed to grow upon melt or cold crystallization and has a 10_3 helical chain conformation. The β form is prepared at high draw ratio and high drawing temperature and is known to take a left handed 3_1 helical conformation, whereas a new γ form produced through epitaxial crystallization. On the crystal structure of α form, there are two main opinions on the chain conformation of PLLA in the unit cell. One is the "pure" 10_3 helix regular (α) and the other is the so-called "distorted" 10_3 helix (ά) conformation owing to the interchain interactions between CH_3 groups.

In the present work, twin screw extruded films of PLLA and PCL homopolymers and 50/50 (w/w) blend were irradiated with gamma rays from Co-60 at doses in the range of 25 to 500 kGy. Wide-angle X- ray diffraction (WAXD) patterns of non irradiated and gamma irradiated samples were obtained to investigate the effects of ionizing radiation on the crystalline structure.

2. EXPERIMENTAL

2.1. Preparation of Blend Sheets

PLLA pellets were dried in a vacuum oven at 90°C and PCL pellets were dried at 40°C overnight to avoid hydrolysis of polymers during the melt-processing. Sheets of PCL and PLLA homopolymers and blend with PLLA/PCL weight ratio of 50/50 were prepared using a twin screw extruder (Labo Plastomill Model 150C, Toyoseki, Japan) equipped with a T-die (60mm width and 1.05mm thickness). 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.

2.2. Thermal Treatment

Annealing was performed for PLLA and blend at 140°C for 30 min at NIMC (Japan). The samples were left inside the turned off oven up to 57°C for the low rate of temperature decrease.

2.3. Gamma irradiation

Samples were irradiated at IPEN–CNEN/SP (Brazil) using a Co-60 irradiator Gammacell model 220, series 142 from Atomic Energy of Canada Limited. Doses of 25, 50, 75, 100 and 500 kGy were applied at a dose rate of 4.3 kGy h^{-1}. Samples were cut $10 \cdot 100$ cm^2, and irradiated at room temperature in air.

2.4. Wide-angle X- ray diffraction (WAXD)

Patterns of non irradiated and irradiated samples with 100 kGy and 500 kGy were obtained using a diffractometer Rigaku Denki Co. Ltd., Multiflex model, Cu Kα radiation.

3. RESULTS AND DISCUSSION

WAXD patterns of non irradiated PCL homopolymer; PCL/PLLA 50/50 blend; PLLA homopolymer as extruded samples are shown in Figures 1, 2 and 3, respectively and of PLLA annealed homopolymer is shown in Figure 4.

Broz *et al* observed that PCL is crystalline [19]. In this work, in Fig. 1 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) reflections, respectively.

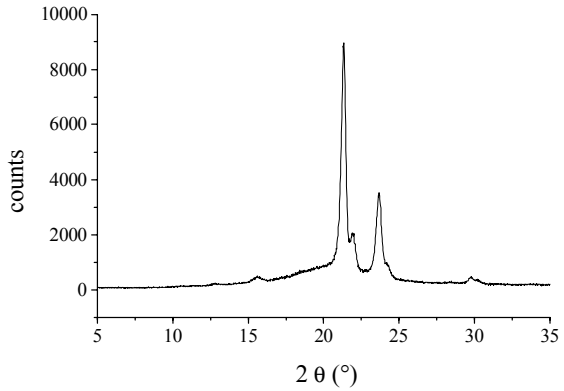

Figure 1. WAXD pattern of non irradiated PCL.

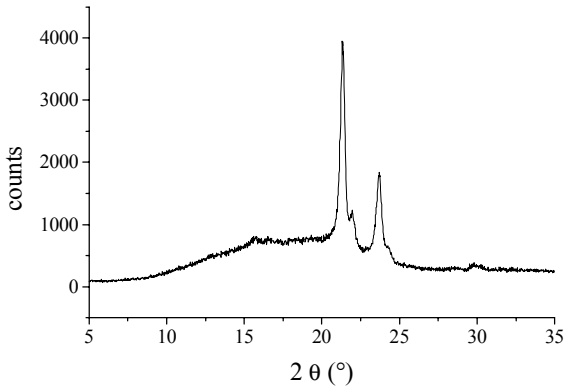

Figure 2. WAXD pattern of non irradiated PCL/PLLA 50/50 (w/w) blend.

In Fig. 2 it is possible to observe the two strongest reflections of PCL and a diffuse scattering due to the amorphous PLLA. [20]. Non irradiated PLLA presents very small peaks in the 2θ 16.4 and 18.7 in a dispersed scattering characteristic of a amorphous phase, Fig. 3. When PLLA is annealed, Fig. 4, it is possible to observe two strong peaks in the 2θ 16.4 and 18.7 and small peak at 22.5°. PLLA as extruded sample is amorphous and crystallizes by thermal treatment.

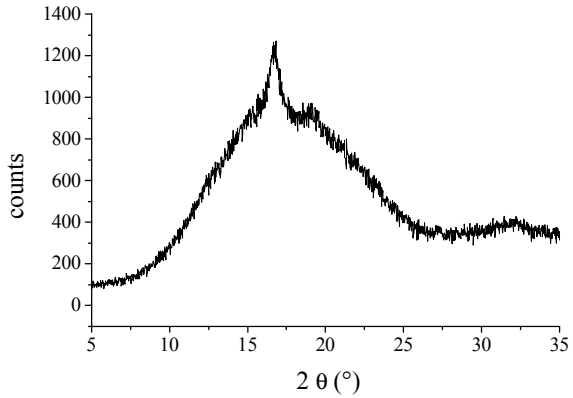

Figure 3. WAXD pattern of non irradiated PLLA.

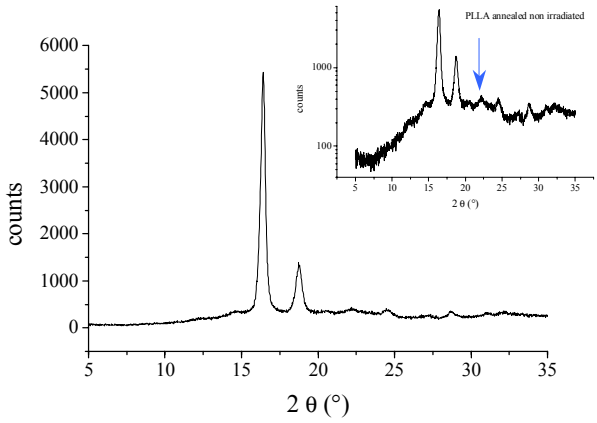

Figure 4. WAXD pattern of PLLA annealed, non irradiated.

By annealing the semi-crystalline polymers at appropriate conditions, the thermal history due to processing can be eliminated and also permits the crystallization to occur. Zhang *et al* [7] studied two different annealing temperatures of PLLA powder samples, 80 and 140 °C, and observed the strongest peaks in the 2θ 16.7 and 19.1 and small peak in 2θ 22.3° for the annealed PLLA powder samples at 140 °C indicating the appearance of phase ά. The same peaks was observed in this work for PLLA sheet annealed at the same temperature, the strongest peaks in the 2θ 16.4 and 18.7 attributed to the (200) and (203) planes and a small peak in 22.5° (indicated by an arrow in the upper figure in Fig. 4, Y axis changed to a logarithm scale) characteristic of phase ά that is not observed for the 80 °C annealed sample.

Fig. 5 and 6 show WAXD patterns of non irradiated and gamma irradiated with 100 and 500 kGy radiation dose PLLA and PCL homopolymers, respectively. 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 500 kGy irradiated samples and the smaller doses were not analyzed in this work.

Kantoğlu *et al* [21] 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 favour 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 [21]. Also, it was observed by Loo *et al* [17] 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 [17]. 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.

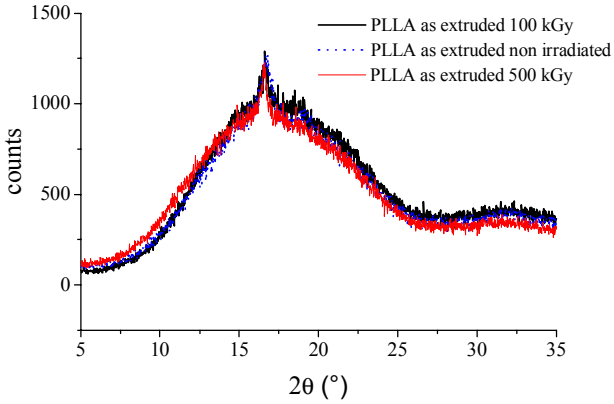

Figure 5. WAXD patterns of as extruded PLLA non irradiated and gamma irradiated with 100 and 500 kGy.

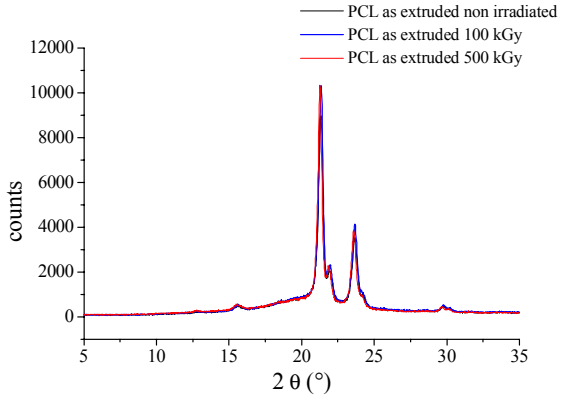

Figure 6. WAXD patterns of as extruded PCL non irradiated and gamma irradiated with 100 and 500 kGy.

In this work, PCL samples, non irradiated and irradiated with 100 and 500 kGy radiation doses, show the two strongest reflections at Bragg angles 2θ =21.4° and 2θ =23.7° that have been attributed in the literature to the (110) and (200) reflections, respectively. For as 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 2θ =16.4° and 2θ =18.7° as described previously in the literature that are attributed to 10_3 (ά-form) distorted helices.

Fig. 7 shows non irradiated and gamma irradiated with 100 and 500 kGy radiation dose PCL/PLLA 50/50 (w/w) blend. An accurate examination of the broad of the X-ray profile indicates same changes related to gamma irradiation.

The disorder in the crystalline domains can be evaluated by measuring the crystallite sizes which are related to the radial widths Δ(2θ) of the reflections at a scattering angle 2θ by the Scherrer equation, Eq. 1.

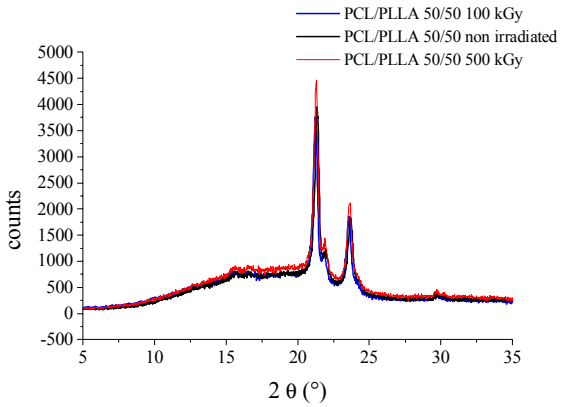

Figure 7. WAXD patterns of as extruded PCL/PLLA 50/50 (w/w) non irradiated and gamma irradiated with 100 and 500 kGy.

In reality, there are two contributions to the width: one is the size and the other is the paracrystallinity or microstrain [22].

The full-width at half maximum (FWHM), B, is related to the mean dimension of crystallites perpendicular to the *hkl* planes, t, by Scherrer's equation [17]:

$$B=0.9\lambda/t\cos\theta \qquad (1)$$

where B is the broadening of diffraction line on the 2θ scale (radians) measured at its half maximum intensity. The FWHM is strongly affected by crystal defects and distortions, which cause line broadening [17]. There, the variation in the FWHM, B, was used as a rough indication of the changes in crystallite size as a function of radiation dose. Table 1 shows the calculated mean crystallite size for PCL and blend of PLLA/PCL. The peak used for the calculation was (200) of PCL.

There is a small increase of the mean crystallite size with increasing radiation dose. Zhu *et al* [23] had observed that the crystallization of radiation crosslinked 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 cross-linking. On the other hand, PLLA presence on the 50/50 blend do not interfere on the observed mean crystallite size increase.

Table 1. Mean crystallite size for PCL and blend of PCL/PLLA 50/50 (w/w).

Sample	Non irradiated	100 kGy	500 kGy
PCL	20.7nm	21.5nm	23.98nm
PCL/PLLA	19.5nm	20.9nm	24.7nm

3. CONCLUSIONS

PCL samples, non irradiated and irradiated with 100 and 500 kGy radiation doses, show the two strongest reflections at Bragg angles $2\theta = 21.4°$ and $2\theta = 23.7°$ that have been attributed in the literature to the (110) and (200) reflections, respectively. For as 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 $2\theta = 16.4°$ and $2\theta = 18.7°$ previously attributed in the literature to distorted 10_3 (α-form) helices. PLLA as extruded samples are amorphous and crystallize by thermal treatment. It was possible to observe slight alteration on the crystallite size of PCL in all irradiated blends in the dose range studied. While WAXD is used to study the orientation of the crystals, and the packing of the chains within these crystals, small-angle X-ray scattering (SAXS) is used to study the electron density fluctuations that occur over larger distances as a result of structural inhomogeneities [21]. Therefore SAXS would be helpful to study the effect of the radiation dose on the structural homogeneity of the homopolymers and blend. It is expected that the degree of crystallization would be affected by the diverse amount of main chain scission induced by the different radiations doses. Therefore, a further use of WAXD will be on the study of thermally treated PLLA irradiated samples, and samples irradiated with doses below 75 kGy.

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