WAXD and FTIR Studies of Electron Beam Irradiated Biodegradable Polymers

Y. Kodama [1], N. B. Lima [1], C. Giovedi [2], L. D. B. Machado [1], W. A. P. Calvo [1], K. Nakayama [3]

[1] Instituto de Pesquisas Energéticas e Nucleares – IPEN–CNEN/SP, Av. Prof. Lineu Prestes 2242, Cidade Universitária, 05508-000, São Paulo, Brazil
[2] Centro Tecnológico da Marinha em São Paulo – CTMSP, Av. Prof. Lineu Prestes 2468, Cidade Universitária, 05508-000 São Paulo, Brazil
[3] National Institute of Advanced Industrial Science and Technology (AIST), Research Institute for Sustainable Chemical Innovation, AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki, 3058565-Japan

Email contact of main author: ykodama@ipen.br

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, 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 cross-linking 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 to 1000 kGy in order to evaluate the effect of electron beam radiation on the homopolymers and blend. 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 FTIR spectra was obtained using a NICOLET 4700, ATR technique, ZnSe crystal at 45°. By WAXD patterns of as extruded non irradiated and irradiated PLLA it was observed 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) was 68% and decreased with radiation dose above 500 kGy. On the other hand. PLLA CI was 10% and increased with radiation dose above 750 kGy. 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 1 MGy the crystallite size of PCL was a little bigger in the blend than the homopolymer. Also it could be observed that the PLLA peak increase at 14.2° was affected by PCL presence on the blend above 750 kGy. 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.

1. Introduction

The non-biodegradable plastic waste has become crucial in recent years especially concerning to environmental impact. 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 characteristic and non toxicity [1,2]. 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 [1]. Not only the 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 [3]. 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 [1].

Ionizing radiation processing of polymers induces polymeric structural changes such as scission and crosslinking [4]. 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 [5]. 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 [6]. 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 [6].

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 extrusion process. Blends were prepared using a twin screw extruder Labo Plastomill Model 50C 150 from Toyoseki, at AIST, Japan. PCL and PLLA homopolymers and PCL:PLLA blend weight ratio of 50:50 were extruded at 10 rpm. The sheets were obtained from a horizontal T-die (60 mm X 1.05 mm). Water bath at room temperature was used to cool the sheets after extrusion, which surface level was 55 mm distant from the T-die. The take up speed was 0.35 m·min^{-1}.

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, 100, 250 500, 750 kGy and 1 MGy were applied at dose rate of 22.4 kGy·s^{-1}.

2.3. FTIR

Samples spectra of attenuated total reflection using infrared Fourier transform (ATR-FTIR) spectroscopy were obtained at CTMSP – SP, 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 sec (first measurements) and 1 sec (subsequent ones); slits DS ½°, SS ½°, KS 0.3mm; 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 [8,9], Eq. 1:

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

2. Results and Discussion

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 [9]. Diffraction patterns of as extruded non irradiated and EB irradiated samples of PLLA homopolymer; PCL:PLLA 50:50 blend; PCL homopolymer samples are shown in Fig. 1, 2 and 3, respectively.
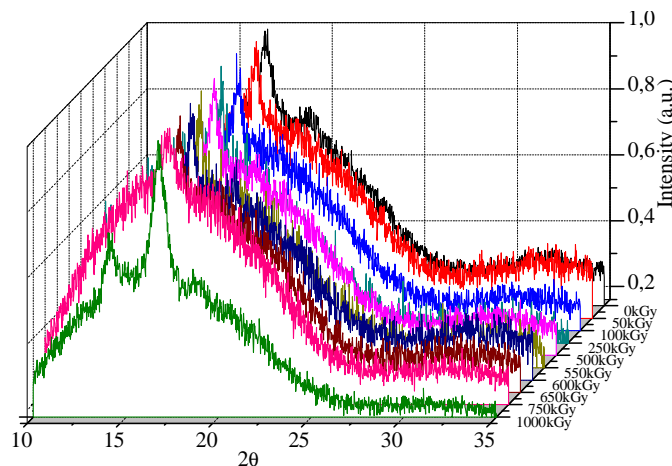

FIG. 1. PLLA irradiated with 0, 50, 100, 250, 500,550, 600, 650, 750 and 1000kGy.

Broz et al observed that PCL is crystalline [10]. 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) 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 [10]. 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, Fig. 1. Only for 1 MGy irradiated PLLA another peak of small intensity appeared at 14.2°.

Kantoğlu et al [12] 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.
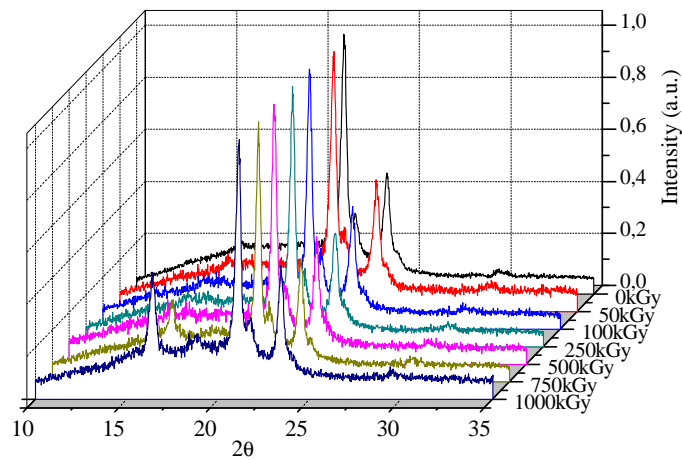

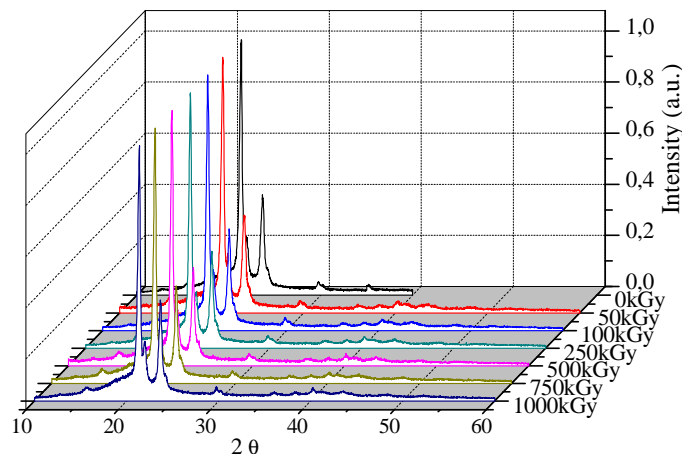*FIG. 2. PCL:PLLA 50:50 irradiated with 0, 50, 100, 250, 500, 750 and 1000kGy.*

FIG. 3. PCL irradiated with 0, 50, 100, 250, 500, 750 and 1000kGy.

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 [12]. Also, it was observed by Loo *et al* [5] 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 [5]. 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 planes, t, is related to the full-width at half maximum (FWHM), B, by Scherrer's equation [5], Eq. 2:

$$t=0.9\lambda/Bcos\theta \tag{2}$$

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 [5]. 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. Table I shows the calculated mean crystallite size for PCL and blend of PLLA:PCL as a function of EB radiation dose. 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 [13] 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 cross-linking. 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 1 MGy 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 1 MGy irradiated samples.

TABLE I: MEAN CRYSTALLITE SIZE (nm) FOR PCL AND BLEND OF PCL:PLLA 50:50 (w:w) AS A FUCTION OF EB RADIATION DOSES.

Dose (kGy) Sample	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

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]. Table II presents the CI values of PCL and PLLA homopolymers non irradiated and EB irradiated. A_T was integrated from 10° to 35°. PCL peaks at 21.5°, 23.7° and 29.8° were used for A_C integration. 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 1 MGy radiation dose.

TABLE II: CRYSTALLINE INDEX CI (%) FOR PCL AND PLLA AS A FUNCTION OF EB
RADIATION DOSES IRRADIATED.

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

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 kGyin the studied range.

The behaviour of polymer blends depends, in general, on the mixing degree of the components and 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 [14]. 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 [6]. Probably this fact occurred on the spectra (A) showed in Fig. 4 that shows FTIR spectrum of non irradiated PCL, PLLA homopolymers and of PLLA:PCL 50:50 (w:w) blend.
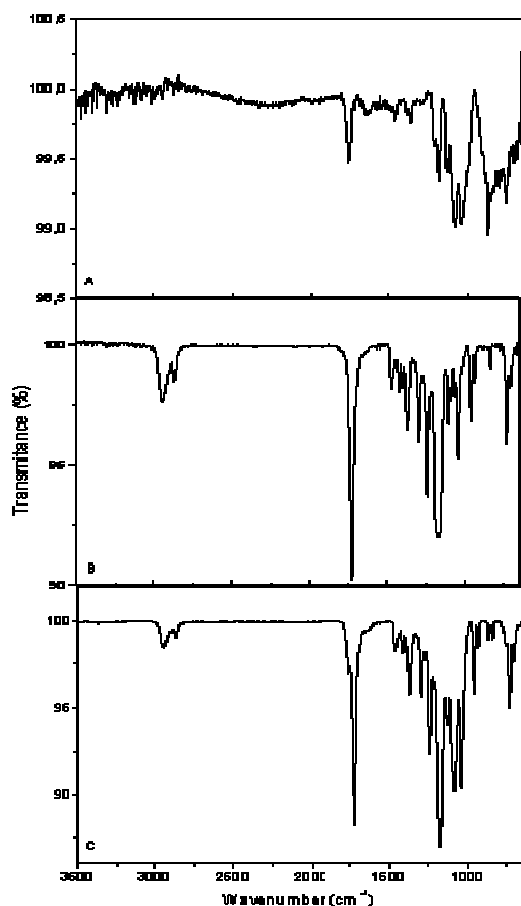

FIG. 4 – FTIR-ATR spectrum of non irradiated A) PLLA, B) PCL, and C) PCL:PLLA 50:50 blend,.
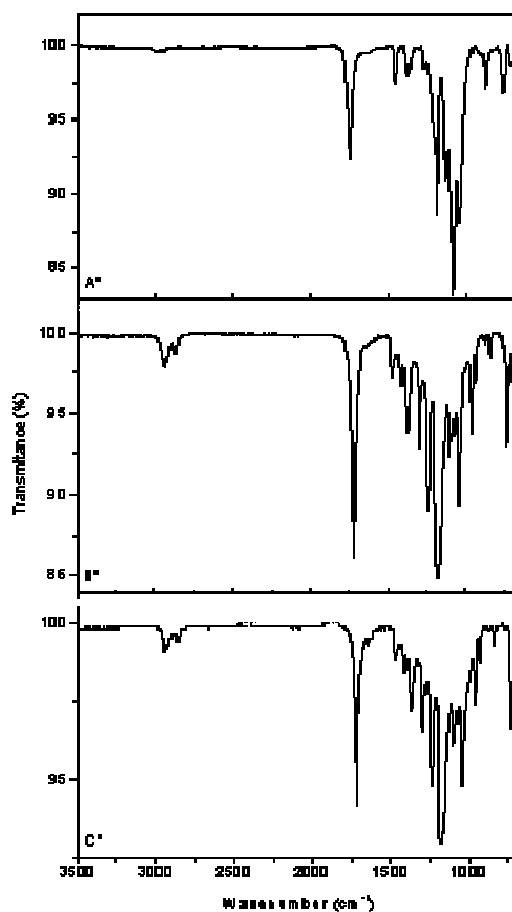
FIG. 5 – FTI-ATRR spectrum of EB irradiated samples of A") PLLA, B") PCL, and C") PCL:PLLA 50:50 blend,

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 incompatible, the spectrum of the blend is simply the spectral sum of the spectra of the two polymers, within experimental error [15]. In the case of PLLA:PCL blend, both components are hydroxy acid polymers, having the same functional groups, as showed in Fig. 4 and 5. The difference between them is the higher amount of CH_2 groups on PCL structure that shows more peaks of absorption at $750 - 1500$ 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 [1].

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 [16]. As a result of the radiation effect, the polymers are subject in varying extents to degradation and cross-linking reactions. Parameters such as morphology, chemical structure of the polymer, dose and irradiation media determine whether cross-linking or chain scission is the dominating effect of the irradiation process [14]. In addition to cross-linking 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 cross-linking by reacting with polymer radicals [17].

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 spectrum with the chemical reactions that have occurred [15]. Maybe because 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 [2]. Although, it has been observed that a new band appeared in the C=O stretching band region $1810-1710$ 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.

3. Conclusion

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. 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 1 MGy 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 CI decreases with radiation dose. On the other hand. PLLA CI increases with radiation dose above 750 kGy.

4. References

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