

Gamma radiation effect on structural properties of PLLA/PCL blends

Y. Kodama ^{a,*}, L.D.B. Machado ^a, C. Giovedi ^b, K. Nakayama ^c

^a Instituto de Pesquisas Energéticas e Nucleares – IPEN–CNEN/SP, Centro de Tecnologia das Radiações, Av. Prof. Lineu Prestes, 2242, CEP 05508-000, São Paulo, Brazil

^b Centro Tecnológico da Marinha em São Paulo – CTMSP, Av. Prof. Lineu Prestes, 2468, Cidade Universitária, 05508-000 São Paulo, SP, Brazil

^c Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology – AIST, Tsukuba, Ibaraki 305-8565, Japan

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Abstract

Poly(L-lactic acid) (PLLA) and poly(ϵ -caprolactone) (PCL) extruded homopolymers and PLLA/PCL blends films were irradiated with gamma rays from Co-60 at doses in the range of 25–500 kGy to investigate the effect of the ionizing radiation on the morphological properties of the samples. The morphology of the homopolymers and the blends were observed by scanning electron microscope (SEM). The micrographs of the fractured homopolymers and blends have shown immiscibility of the blends. The crystallization of PLLA can be observed in the annealed samples. Samples irradiated with 100 kGy presented few variations in the morphology. But in PCL homopolymer and PCL/PLLA 50/50 wt% blend irradiated with 500 kGy dose it was possible to observe significant alteration. The ruptured sample surface of irradiated PCL with 500 kGy became full of scales probably due to an increase of crosslinking density induced by the ionizing radiation, but apparently no changes promoted by ionizing radiation could be observed on the irradiated PLLA by SEM.
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1. Introduction

The problem of non-biodegradable plastic waste remains a challenge due to its negative 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 characteristics and non-toxicity [1–7]. Poly(lactic acid) (PLLA) is a poly(α -hydroxy acid) and poly(ϵ -caprolactone) (PCL) is a poly(ω -hydroxy acid) [1]. PLLA is a hard, transparent and crystalline polymer [8]. On the other hand, PCL can be used as a polymeric plasticizer because of its ability to lower elastic modulus and to soften other polymers [2].

To improve some desirable properties two or more polymers can be mixed to form polymeric blends [9]. 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 poor adhesion between phases [3]. Chemical structure influences the biodegradation of solid polymers [4]. Enzymatic and non enzymatic degradations occur easier in the amorphous region [8,10–15]. The morphology of the blends affects the thermomechanical properties [14,16] as well as the biodegradation of the polymers [11,12]. So the control of the morphology of an immiscible polymer processed by melting is important for the tailoring of the final properties of the product [3].

Moreover, both polymers PLLA and PCL can be used in biomedical applications, which require a proper sterilization process. Nowadays, the most suitable sterilization

* Corresponding author. Tel.: +55 11 3816 9292x271; fax: +55 11 3816 9186.

E-mail address: ykodama@ipen.br (Y. Kodama).

method is high energy irradiation [6,17]. However, polymeric structural changes such as scission and crosslinking are induced by radiation processing of polymers [17]. In this paper, it was studied the morphological changes in these two polymers and their blends on irradiation with gamma radiation.

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 homo-polymers and blends with PCL/PLLA weight ratio of 25/75, 50/50 and 75/25 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). T-die temperature was set at 205 °C for PLLA homo-polymer 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. Dynamic mechanical analysis (DMA)

Dynamic viscoelasticity properties of non-irradiated PCL/PLLA blends were measured as a function of temperature by a non-resonant forced vibration type apparatus, Rheovibron DDV-III-EA, from Orientec Co. The frequency utilized was 35 Hz. The temperature range used was from -150 to 250 °C with the rate of increase of 1 °C min⁻¹.

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 × 100 cm² and irradiated at room temperature in air.

2.4. Scanning electron microscopy (SEM)

Morphology of the fractured surfaces of the non-irradiated homopolymers and blends was examined by a scanning electron microscope (SEM) DS-720 TOPCON Co. The photomicrographs of the fractured surface of the blends sheet were taken after cryogenic fracture and 4–5 min gold coating.

SEM micrographs of the irradiated homopolymers and blends sheets surfaces from fractured samples were obtained using a scanning electron microscope model JXA-6400 (JEOL).

3. Results and discussion

In general, the morphology results from the complex thermomechanical history experienced by the different constituents during processing. So, parameters like the composition, viscosity ratio, shear rate/shear stress, elasticity ratio and interfacial tension among the component polymers, as well as processing conditions such as time, temperature and type of mixing, rotation speed of rotor of mixing determine the final size, shape and distribution of dispersed phase during the melting process [3,15,18]. Moreover, the structural modifications induced by ionizing radiation may alter the morphology of the samples. SEM micrographs of fractured surfaces of non-irradiated as extruded samples are shown in Fig. 1. As extruded PCL micrograph shows a

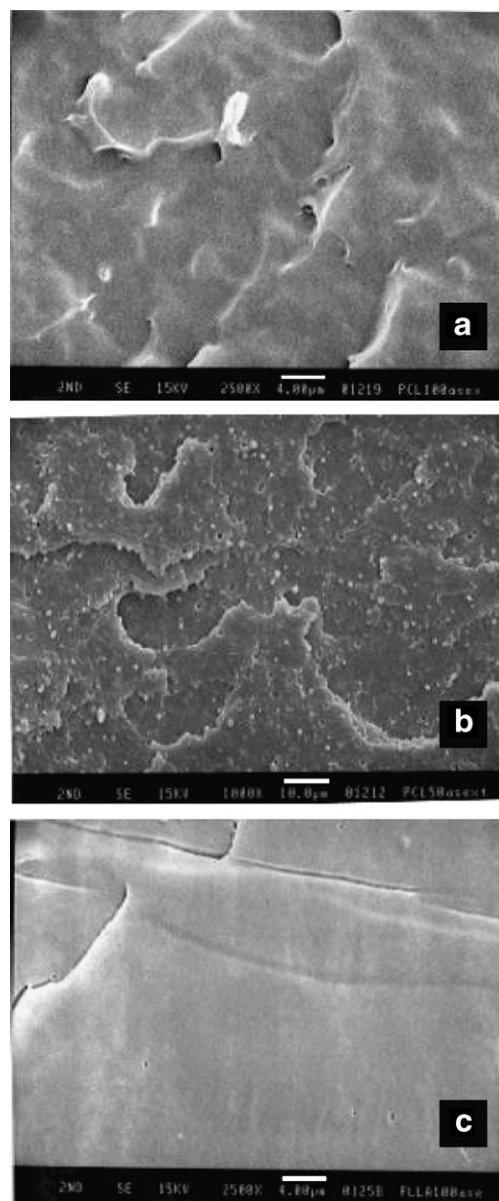


Fig. 1. SEM micrographs of non-irradiated as extruded (a) PCL (b) PCL/PLLA 50/50 blend and (c) PLLA.

homogeneous morphology, Fig. 1(a). The as extruded PCL/PLLA 50/50 micrograph shows spheres with different sizes and shapes. It is possible to observe the continuous PLLA-rich phase and the PCL-rich dispersed phase with a maximum domain size of 1.5 μm , as visualized before by Tsuji et al. [15] in PCL/PLLA solution-cast blends. The PCL-rich phase is homogeneously dispersed in the PLLA matrix, Fig. 1(b) and Fig. 3(b). One can observe some cracks or voids in the PLLA film probably caused by the temperature of processing, Fig. 1(c). It has mentioned before that the degradation of aliphatic polyesters can occur because of melting at high temperatures [5,19].

Micrographs of annealed PLLA, PCL and PCL/PLLA 50/50 are shown in Fig. 2. After annealing, changes in the morphology due to the crystallization of PLLA are observable in Fig. 2(b). Utracki [9] explained that depending on the crystallization conditions various types of morphology can be obtained, which proceeds through melt, nucleation, lamellar growth and, spherulitic growth. Although the temperature of annealing is lower than the PLLA melting temperature (T_m), the thermal treatment has allowed the PLLA to crystallize. Moreover, even though as extruded and annealed samples temperatures of processing were the same, one can observe the reduction of the cracks on the PLLA annealed sample. It is also possible to observe some morphological changes. The spheres are apart from the matrix and in addition the matrix was changed due to the crystallization of PLLA as shown Fig. 2(a). The blends are not miscible and the after extru-

sion cooling from the melt to room temperature causes the phase separation due to the difference between the melting temperatures of both blend components, PCL and PLLA. In preliminary studies by differential scanning calorimetry (DSC) no change in the PLLA melting temperature was observed by increasing the PCL content in the blends. It can be observed that, as PCL amount increases, PCL T_m peak increases in the region of the glass transition temperature of PLLA [19]. Although the immiscibility is there, it is possible to observe by SEM some interfacial interaction, as the spheres seem to be covered by a thin layer of the polymeric matrix of the blends, Fig. 1(b). It should be noted that the blends were well mixed during extrusion as shown by the distribution and the size of the spherulites in the matrix. Dell'Erba et al. [3] have found that it was reasonable to assume that low interfacial tensions were obtained in PLLA/PCL blends because of their similar chemical nature of the blends components, which allows interpolymer polar interactions across phase boundaries, thus favouring a well-dispersed morphology. Preliminary studies have shown that although both are semi-crystalline polymers, only PCL crystallizes during extrusion. PLLA is amorphous and crystallizes after annealing, which was observed by X-ray diffraction of the non-irradiated samples [17]. Also the orientation of crystallites in the blends was observed by X-ray diffraction, PLLA crystallizes in the α form with 10_3 helical conformation [7]. The thermal treatment increases the quantity of spheres and in Fig. 2(a) it is possible to see some ellipsoids. This suggests that the new spherulites were formed due to the crystallization of amorphous PLLA, as observed previously [17]. In this case, the segregation is also clear. It is possible to observe the separated spheres from the matrix and the cavities. It was discussed in literature [3] that the PLLA spherulites growth mechanism does not change when different amounts of PCL are present in the blend. Additionally, the presence of PCL enhances the PLLA crystallization rate, suggested to likely occur through the increase in the nucleation rate, it was observed that the presence of PCL domains in the PLLA matrix causes a small lowering in the half time of crystallization [3]. Furthermore, the results indicated that even though PLLA and PCL are immiscible, revealed by the presence of two glass transition temperatures for the blends very close to those found for pure PLLA and PCL, they are not highly incompatible [3]. The binary mixture of (two) polymers is considered a compatible blend, when a homogeneous solid system is formed, without phase separations. It means a complete mutual solubility of the two polymers in molten state as well. This compatibility is reflected in, among other physical and mechanical properties, the fact that the system will have one single glass transition temperature (T_g) [20].

Studies from non-irradiated samples by dynamic mechanical analysis (DMA) have shown the stepwise storage modulus (E') decrease with increasing PCL content for isotropic and anisotropic blends, shown in Fig. 3(a). Also it was observed the cold crystallization of PLLA has affected

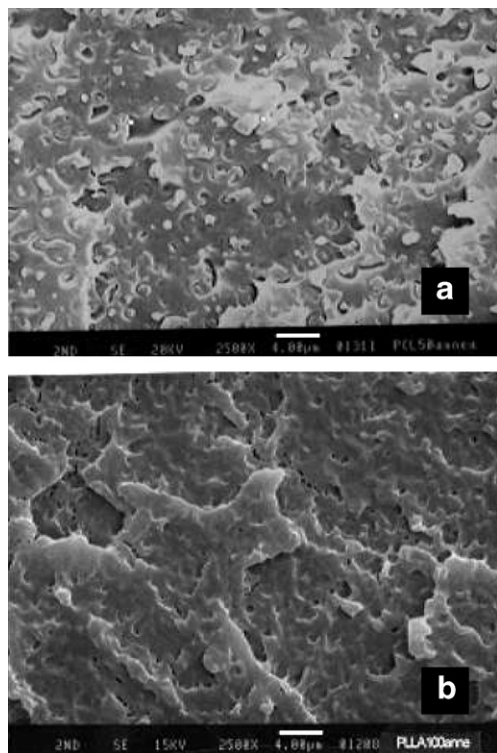


Fig. 2. SEM micrographs of non-irradiated annealed (a) PCL/PLLA 50/50 blend and (b) PLLA.

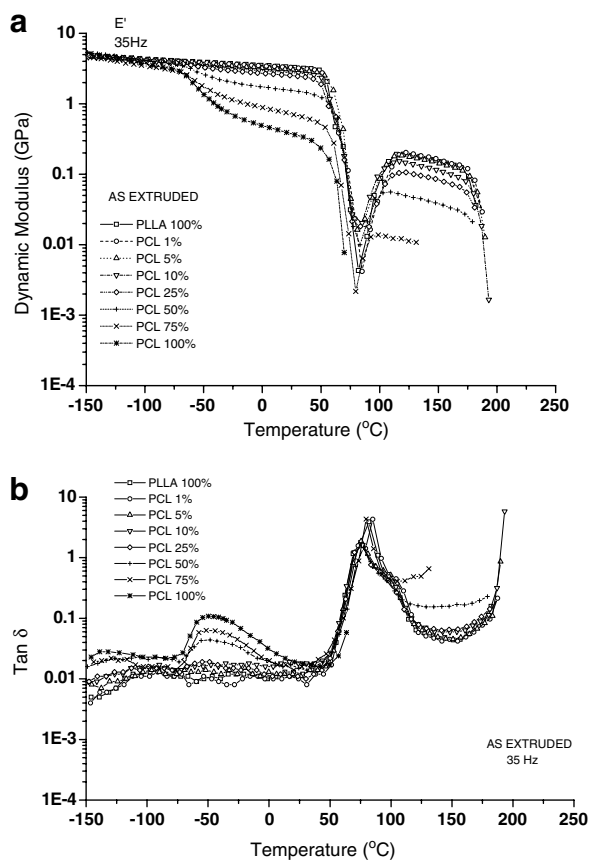


Fig. 3. Temperature dependence of (a) dynamic storage modulus (E') and (b) loss tangent ($\tan \delta$) from as extruded PLLA and blends containing 1%, 5%, 10%, 25%, 50%, 75% or 100% of PCL by weight.

the E' decrease for the as extruded samples. After PCL melting, around 60 °C, one can observe a sudden decrease of E' for the PLLA/PCL blends and after that E' increases due to the PLLA cold crystallization, following decreases again on PLLA melting. It was observed in earlier studies [3] by differential scanning calorimetry that PLLA/PCL melt-quenched blends show PLLA cold crystallization exotherms, while there was no evidence of any PCL cold crystallization. By the loss modulus (E'') curves, shown in Fig. 3, it was possible to observe the glass transition temperature regions of both PLLA and PCL, confirming the immiscibility of blends. Yoshii et al. [5] observed that E' of non-irradiated PCL dropped rapidly at above melting temperature, in contrast to the irradiated with 30 kGy sample that showed a steady decrease up to 220 °C attributed to branch structures formed during irradiation.

Figs. 4 and 5 show micrographs of PCL and PLLA homopolymers and PCL/PLLA 50/50 blend irradiated with 100 kGy and 500 kGy, respectively. Comparing the SEM micrographs shown in Figs. 4(a) and 1(a), it is observed very few changes on the surface of ruptured samples. In earlier studies by size exclusion chromatography of electron beam irradiated PCL in air, it was observed a small increase followed by a decrease of crosslinking degree up to 5 kGy and after that an increase of gel-content of

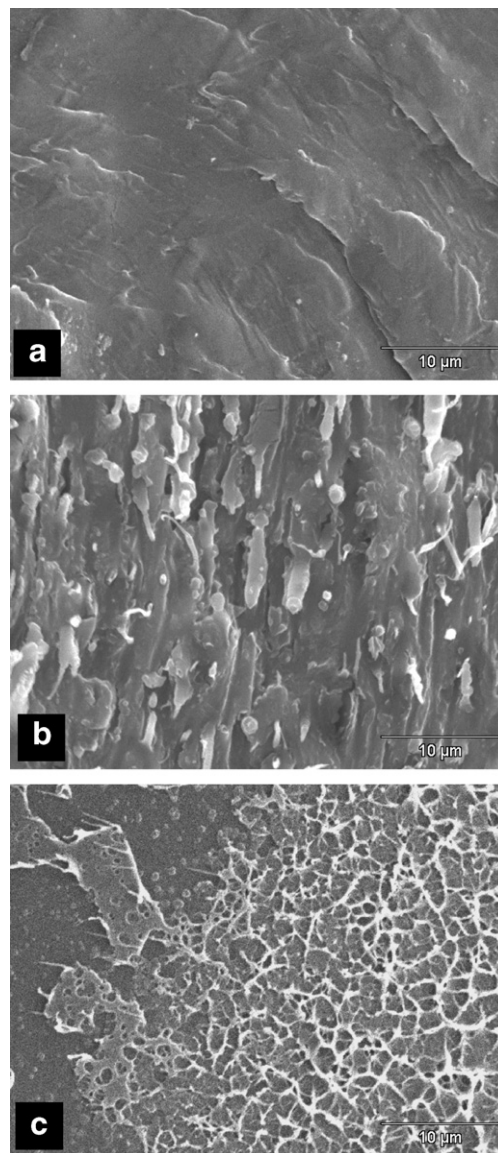


Fig. 4. SEM micrographs of as extruded samples after gamma irradiation up to 100 kGy (a) PCL (b) PCL/PLLA 50/50 and (c) PLLA.

15 wt%, indicating the enhance of crosslinking degree up to 200 kGy radiation dose [21]. Even though PCL crosslinking predominates at radiation doses higher than 5 kGy and random chain-scission at lower doses [21,22], in this paper, only few changes could be seen by SEM for the irradiated PCL up to 100 kGy. However, Fig. 5(a) shows that the ruptured sample surface of irradiated PCL with 500 kGy became full of scales suggesting that the increase of crosslinking density induced by the ionizing radiation causes this alteration.

In Fig. 4(c) it is observed that the surface of PLLA sample became rough. This fact is correlated to chain-scissions promoted by gamma radiation. In the literature it was observed that PLA mainly undergoes chain-scissions at doses below 250 kGy. At higher doses of radiation, crosslinking reactions increase as a function of the increasing radiation dose. The reactions occur in the amorphous

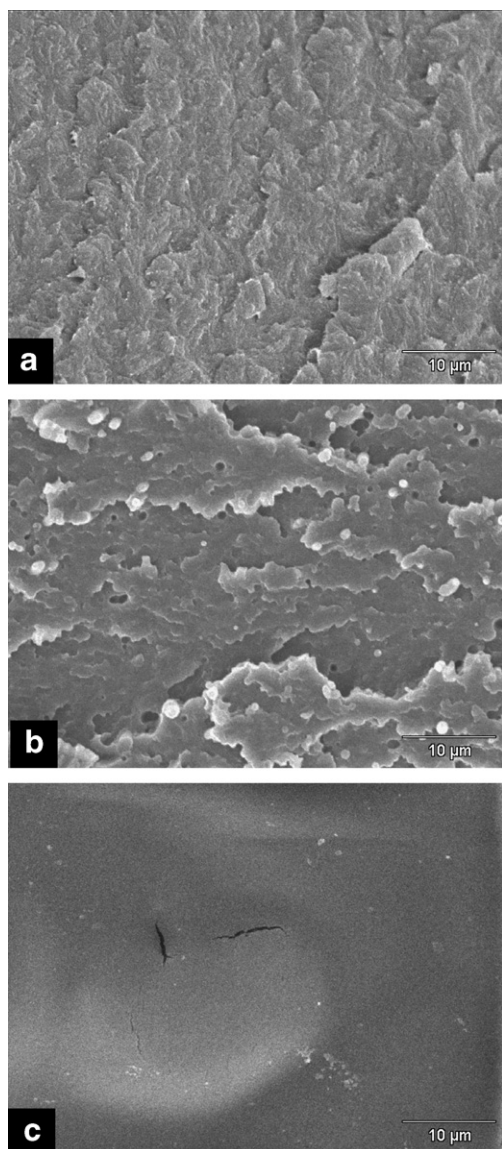


Fig. 5. SEM micrographs of as extruded samples after gamma irradiation up to 500 kGy (a) PCL (b) PCL/PLLA 50/50 and (c) PLLA.

phase of the polymer [21]. Samples submitted to doses in the range of 30 up to 100 kGy showed a marked depression in mechanical properties attributed to oxidative chain-scissions in amorphous region [23]. Comparing Figs. 5(c) to 1(c), apparently no changes are visible by SEM on the irradiated PLLA with 500 kGy radiation dose, in contrast to the observed previously in the literature in other properties [21–23].

It seems that the ionizing radiation induced some shape alteration in the PCL dispersed phase in blends that were irradiated with 100 kGy. Likewise, samples submitted to irradiation processing up to dose of 500 kGy present the matrix with decreased PCL spherulites disperse phase, suggesting that some interaction between both polymeric phases had been promoted by the ionizing radiation. Previous studies demonstrated that gamma radiation does not affect significantly thermal properties of the blends when

doses were kept below 75 kGy. A small decrease of PLLA T_m occurred probably due to PLLA main chain-scission. Thermal treatment induces PLLA T_m variation on irradiated blends with high concentration of PLLA. The crystallinity of PCL homopolymer and PLLA homopolymer as well as in the studied blends was not significantly affected by irradiation up to 100 kGy [19]. On the other hand, after irradiation with higher doses, PCL samples were more thermally stable than PLLA and blend [23]. Thermal properties of PLLA were not affected by gamma radiation up to 100 kGy [24]. Other results obtained previously by Kodama et al. [25] have shown that both, gamma and EB radiation, at doses up to 500 kGy, do not cause sample degradation to any significant extent to be detectable by FTIR. As well, the miscibility of the polymeric blends was not affected by the irradiation process [25].

4. Conclusion

The SEM micrographs of the fractured homopolymers and blends have shown their immiscibility. The crystallization of PLLA could be observed on the annealed samples. Even supposing that the structural modifications induced by ionizing radiation may alter the morphology of the samples. Samples irradiated with 100 kGy presented little variation on the morphology. It seems that some shape alteration in the PCL dispersed phase in blends occurred. Likewise, samples submitted to irradiation processing up to dose of 500 kGy presented the matrix with decreased PCL spherulites disperse phase, suggesting that some interaction between both polymeric phases had been promoted by the ionizing radiation. However, in PCL homopolymer and PCL/PLLA 50/50 irradiated with 500 kGy samples it was possible to observe significant alteration. The ruptured sample surface of irradiated PCL with 500 kGy became full of scales probably due to an increase of crosslinking density induced by the ionizing radiation. The surface of PLLA sample became rough with 100 kGy radiation dose correlated to chain-scissions promoted by gamma radiation. On the other hand, apparently no changes are visible by SEM on the irradiated PLLA with 500 kGy radiation dose, in contrast to the observed previously in the literature.

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