FTIR INVESTIGATION OF IRRADIATED BIODEGRADABLE BLENDS

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ABSTRACT

PLLA and PCL have been receiving much attention due to their biocompatibility, non toxicity and biodegradability in human body as well in the earth. PLLA is a hard, transparent and crystalline polymer while PCL decreases elastic modulus and softens polymers, acting as a polymeric plasticizer. Both polymers were mixed in order to form blends to improve some desirable properties. According to the literature, 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. Two commercial biodegradable polymers, PCL and PLLA, blends and the homopolymers were irradiated with gamma rays from Co-60 and electron beam at doses in the range of 25 to 500 kGy in order to evaluate the effect of gamma and electron beam radiation on the blends. The results have showed that the ionizing radiation does not promote degradation of the studied homopolymers and blends and, do not affect the miscibility of the blends.

Key-words: FTIR, PLLA, PCL, biodegradable polymer, gamma radiation.

INTRODUCTION

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, environmental friendly characteristic and non toxicity[1-6]. Poly (lactic acid) (PLLA) is a poly (α-hydroxy acid) and poly (ε-caprolactone) (PCL) is a poly (ω-hydroxy acid)[1].

Two or more polymers can be mixed to form polymeric blends to improve some desirable properties and/or for economical reasons. A twin-screw extruder is a continuous mixer from which the blend quality and run-to-run reproducibility are satisfactory [7]. PLLA is a hard, transparent and crystalline polymer[8]. On the other hand PCL decreases elastic modulus and softens polymers, so it can be used as a polymeric plasticizer associated to polymers[2].

Not only the chemical structure influences the biodegradation of solid polymers, but also the presence of highly ordered structures[8-11]. Enzymatic and non enzymatic degradation occur easier in the amorphous region[8, 12, 13].

In the present work, biodegradable PLLA/PCL blends of various compositions obtained using a twin screw extruder were irradiated with gamma rays from Co-60 in order to evaluate the effect of the ionizing radiation on the chemical structure of the samples by FTIR.

MATERIALS AND METHODS

Preparation of blends

PLLA was dried in a vacuum oven at 90^{o}C and PCL at 40^{o}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 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 in the “hungry state” at 10 rpm. The sheets were obtained from a horizontal T-die (60 X 1.05 mm). Water bath at room temperature was used to cool the sheets after extrusion, which surface level was at 55 mm distant from the T-die. The take up speed was 0.35 m min^{-1}.

FTIR films

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

Gamma irradiation

Samples were irradiated at CNEN/IPEN-SP, Brazil, using the Co-60 irradiator Gammacell model 220, series 142 from Atomic Energy of Canada Limited. Doses of 50, 100, 150, 200 and 500 kGy were applied at dose rate of 4.3 kGy h^{-1}.

Electron beam irradiation

Samples were irradiated at CNEN/IPEN-SP, Brazil, using the electron beam acelerator Dynamitron (E = 1.5 MeV) from Radiation Dynamics, Inc. Doses of 50, 100, 150, 200 and 500 kGy were applied at dose rate of 22.37 kGy s^{-1}.

FTIR analysis

Samples spectra were obtained at CTMSP – SP, Brazil, using a FTIR spectrophotometer NICOLET 4700, by ATR technique with ZnSe crystal device at 45^{o}.

RESULTS AND DISCUSSION

FTIR spectroscopy can be used to establish the nature and level of molecular interactions of blends. The behavior 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[14]. Figure 1 shows FTIR spectrum of non irradiated PCL, PLLA homopolymers and of PLLA:PCL 50:50 blend.

A widely used technique for the analysis of polymer samples with low transmission is the internal reflection spectroscopy or often called attenuated total reflection (ATR). One problem of ATR is the inability to obtain a reproducible pressure and contact area between the sample and crystal[14]. Probably this occurred on the spectra A showed in Figure 1.

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[14]. In the case of PLLA/PCL blend, both components are hydroxy acid polymers, having the same functional groups, as showed in Figures 2 and 3. 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, only intensity modifications, PLLA and PCL seems to be a compatible blend and, in fact they are immiscible[15] .

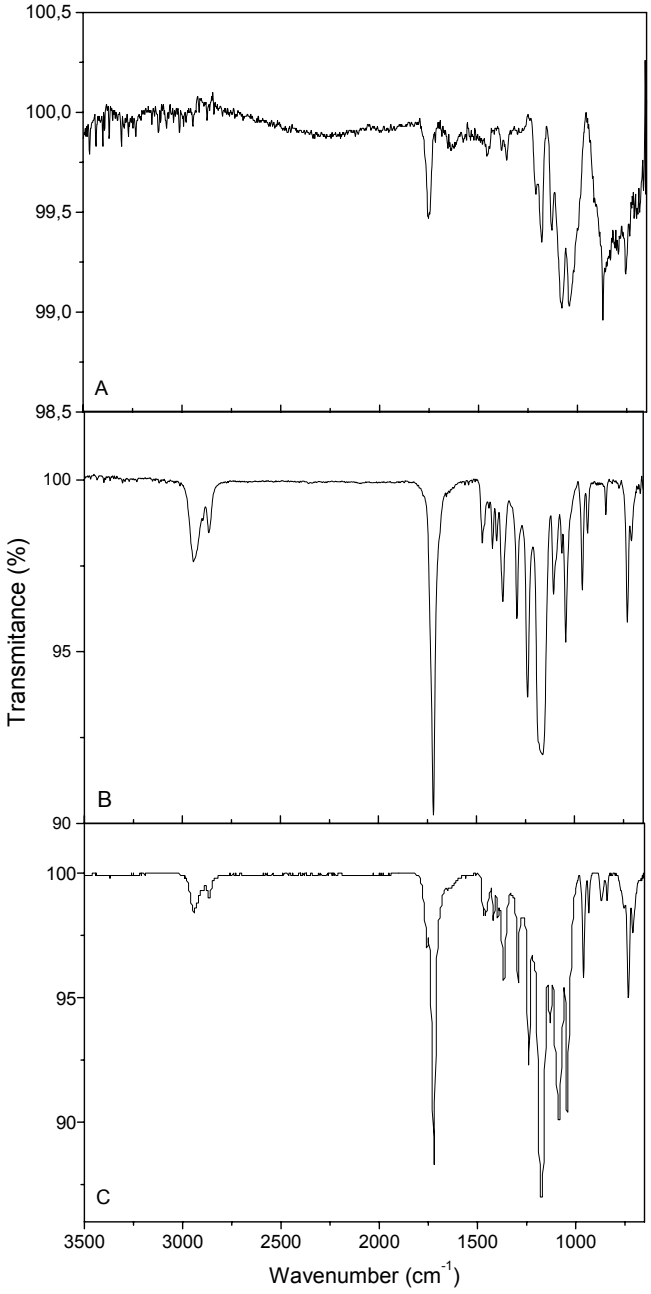

Figure 1 - FTIR spectrum of A) PLLA and B) PCL homopolymers and C) PCL:PLLA 50:50 blend, non irradiated.

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] .

In Figure 2 it is shown the possible radical formed for γ-irradiated PLLA, according to the literature[17]. On the other hand, Figure 3 shows the probable radical formed in EB irradiated PCL samples.

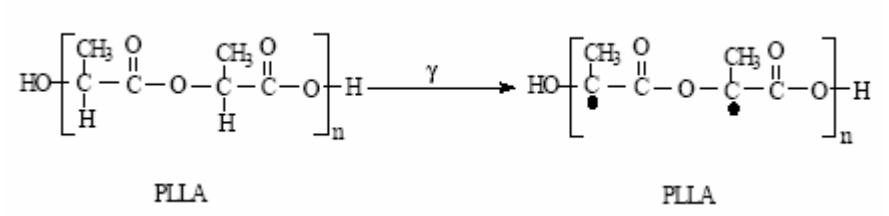

Figure 2 – Possible radical specie formed in PLLA irradiated samples[17].

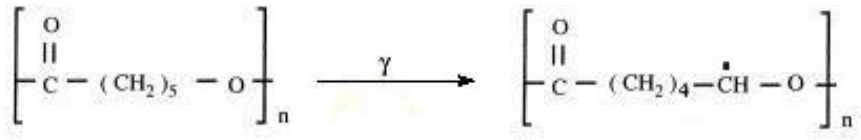

Figure 3 – Probable radical specie formed in PCL irradiated samples[18].

As exposed before, it is expected to observe some modification on functional groups of the irradiated PCL and PLLA homopolymers and blends by FTIR.

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[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[19].

Due to the fact that IR bands of polymers are inherently broad and weak, it is very difficult to detect minor chemical changes occurring on the polymer chain. 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[14]. Maybe due to the fact that it is difficult to obtain reproducible spectra by ATR technique, 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. 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 Figures 4 and 5, respectively.

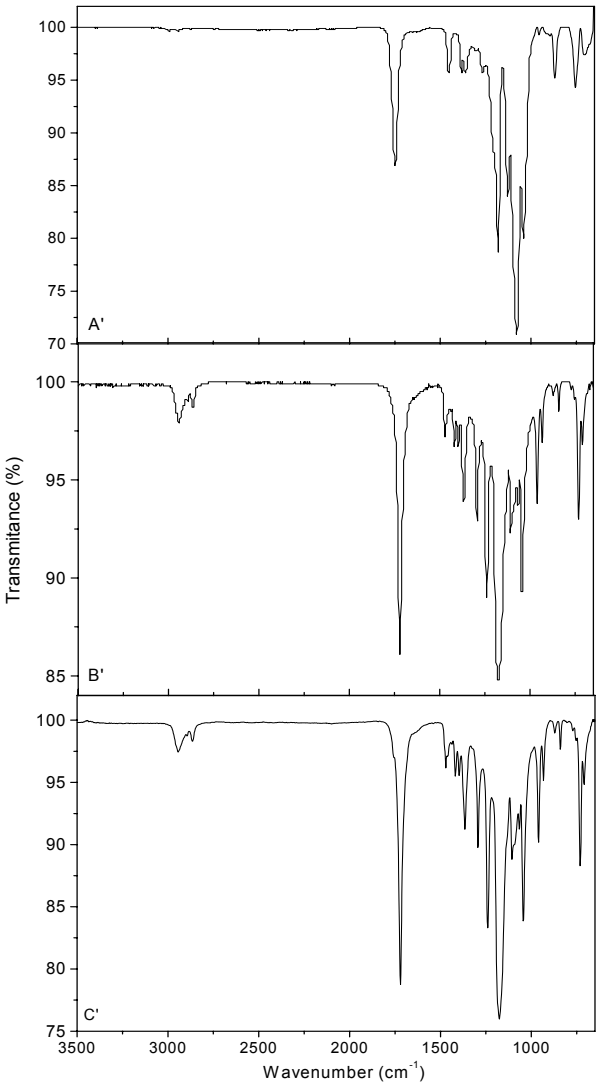

Figure 4 – FTIR spectrum of A') PLLA and B') PCL homopolymers and C') PCL:PLLA 50:50 blend, gamma irradiated.

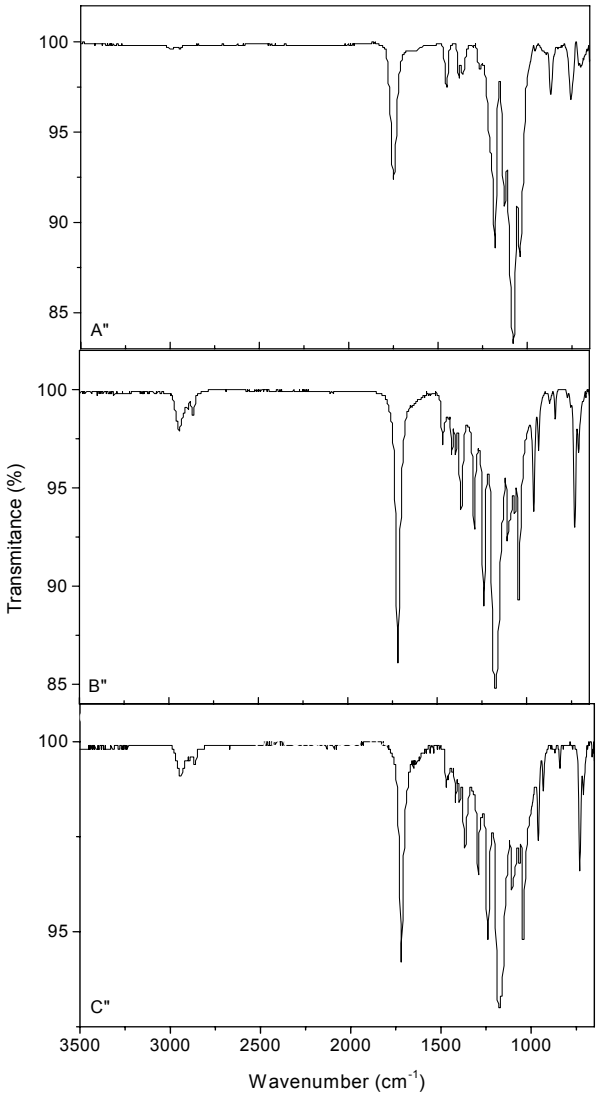

Figure 5 - FTIR spectrum of A") PLLA and B") PCL homopolymers and C") PCL:PLLA 50:50 blend, EB irradiated

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 [16]. In this case both gamma and EB radiation do not cause polymer degradation in significant extent as seen by FTIR. As well, the miscibility of the polymer blends was not affected by the irradiation. Also, it was not possible to evaluate by FTIR the influence of the dose rate on the irradiated polymers without making any spectrum treatment.

As the organization of the polymeric structure affects the biodegradability, in the literature FTIR was used to evaluate possible changes in the PLLA crystallinity[6]. Although, it was 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. They ascribed the 955 cm^{-1} band to an amorphous band and the 921 cm^{-1} band to 10_3 helix associated to the crystalline form. However, in this case it was not possible to observe by FTIR any alteration promoted by the ionizing radiation.

CONCLUSION

In this case both gamma and EB radiation do not cause polymer degradation in significant extent observed by FTIR, 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, the miscibility of the polymer blends was not affected by the irradiation. and, additionally to FTIR other techniques like thermal analysis or scanning electron microscopy would be necessary to evaluate the blend compatibility in the investigated blend compositions.

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