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THERMAL PROPERTIES OF GAMMA IRRADIATED BLENDS BASED ON ALIPHATIC POLYESTERS

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ABSTRACT

Biodegradable polymer is a polymer in which a deleterious change in its properties due to a change in the chemical structure is mediated at least partially by a biological system [1]. Poly(L-lactic acid) (PLLA) and poly(ε-caprolactone) (PCL) have received much attention due to their biocompatibility, non toxicity and biodegradability in human body as well as in the soil [2-4]. According to the literature, PCL homopolymer cross-linking increases with increasing doses of high energy radiation. On the other hand, the irradiation of PLLA homopolymer causes mainly chain-scissions at doses below 250 kGy [5].

In the present work, biodegradable poly(L-lactic acid) and poly(ε-caprolactone) blends films of various compositions were obtained using a twin screw extruder. PLLA/PCL blends and also homopolymers were irradiated with gamma rays from Co-60 at doses in the range of 25 to 100 kGy to investigate the effect of the sterilization processing (according to ANSI/AAMI/ISO 11137 -1994) [6] on the thermal properties of the samples. Differential scanning calorimetric (DSC) curves of non-irradiated and irradiated samples were obtained in the temperature range from –100°C to 200°C, to observe the glass transition, crystallization and melting behavior of the samples as a function of the irradiation process.

1. INTRODUCTION

Aliphatic polyesters which have hydroxy acids, HO-R-COOH, as repeating units are poly (hydroxy acid) or polyhydroxyalkanoate. Hydroxy acids are classified into α-, β- and ω-hydroxy acids depending on the bonding position of the OH group from the COOH ending group. According to this classification, poly (lactic acid) (PLLA) is a poly (α-hydroxy acid) and poly (ε-caprolactone) (PCL) is a poly (ω-hydroxy acid) and their structures can be respectively represented as shown in Fig. 1.

PLLA and PCL have been receiving much attention due to their biocompatibility, non toxicity and biodegradability in human body as well in the soil [2-4]. Biodegradable polymer is a polymer in which a deleterious change in its properties due to a change in the chemical structure is mediated at least partially by a biological system [1].

PLLA PCL

Figure 1. Structures of poly (lactic acid) and poly (ε-caprolactone).

Two or more polymers can be mixed to form polymeric blends to improve some desirable properties and or for economical reasons. One of the several ways to prepare blends is by mechanical mixing. 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 lowers modulus and softens polymers, so it can be used as a polymeric plasticizer in various polymers [3].

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

The aim of this work was to investigate the thermal properties of non-irradiated and gamma irradiated blends consisting of two commercial biodegradable polymers, PCL and PLLA.

2. EXPERIMENTAL

2.1. Preparation of blends

Poly (hexano-6-lactone) PCL from Union Carbide Corporation trade name TONE® P-787. PCL is a linear aliphatic polyester resin, tough, number-average molecular weight (Mn) of about 80,000. Tm = 60°C and Tg = -60°C.
PLLA from Shimadzu Tm = 178°C and Tg = 68°C (pellets).

PLLA was dried in a vacuum oven at 90°C and PCL at 40°C overnight to eliminate the humidity in order to avoid hydrolysis during extrusion. Blends were prepared using a twin screw extruder Labo Plastomill Model 50C 150 from Toyoseki. The homopolymers PCL and PLLA and blends with weight ratio PCL:PLLA 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 1,05mm). A 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. Take up speed was 0.35 m/min.

2.2. 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 25, 50, 75 and 100 kGy were applied at dose rate of 4.3 kGy/h

2.3. Thermal Analysis

A differential scanning calorimeter DSC-50 from Shimadzu was used to evaluate thermal properties of non-irradiated and irradiated homopolymers and blends. Samples with mass in the range of 11 to 13 mg were put in sealed aluminum pans. N_2 was used as the purge gas at a 50 mL/min flow rate. All samples were heated at 10°C/min from –100 to 200 °C. Then, the samples were cooled again to –100 °C and the heating process repeated.

Values of the enthalpy of fusion were calculated from the areas of the corresponding peaks, and melting points were obtained from the temperature at maximum of the peak. The normalized crystallinity of PLLA was calculated by rating the difference between enthalpies of melting and crystallization peaks to the reference melting enthalpy of the 100% crystalline PLLA. The crystallinity of PCL calculated by rating the melting enthalpy of the sample to the reference melting enthalpy of the 100% crystalline PCL. The heat of melting of 100% crystalline PCL and PLLA are, respectively, 135.68 J/g [16] and 93.7 J/g [3,17].

3. RESULTS AND DISCUSSION

The Fig. 2A shows the DSC curves of the homopolymers and 50:50 PCL:PLLA blend from non-irradiated samples. The PLLA homopolymer curve shows several thermal events identified by a, b, c, and d, where (a) represents the glass transition temperature (T_g) followed by an endothermic peak of relaxation; (b) represents the cold crystallization (T_{cc}); (c) is the re-crystallization upon melting and (d) the melting (T_m) of PLLA homopolymer. The DSC curves of the first heating from pure PLLA, Fig. 2.A, show T_m, at 175 °C. As PCL content in the blend increases, it can not be observed any significant variation of PLLA melting temperature. Thermal processing does not affect PLLA T_m as well, Fig. 2B. The cold crystallization indicates that PLLA is amorphous and undergoes to re-crystallization upon heating at 160°C, Fig. 2.A. T_g can be observed in the first and second heating, Fig. 2.B. It can not be observed any change in the PCL T_m by increasing PCL content in the blends, it seems that the blends are not miscible. It can be observed that as PCL amount increases, PCL T_m peak increases in the PLLA T_g region. The very small variation of PCL melting peak temperature is proportional to the increasing amount of this component in the blend.

Irradiation does not influence significantly PCL T_m in the blends. Although it had been observed before that in PCL homopolymer occurs cross-linking and main chain-scissions simultaneously with doses up to 100 kGy [5, 14], it was not possible here to observe any influence on PCL using DSC analysis. However, thermal process decreases PCL T_m in the non irradiated and irradiated blends by around 10 °C, Fig. 2.B and 3.B.

Irradiated blends with high amount of PLLA present PLLA T_m variation by thermal treatment effect, that was observed comparing curves from first and second heating. Concerning the irradiation process, it could be observed that the T_m of PLLA decreases with increasing irradiation dose, probably due to the fact that poly(lactide) mainly undergo chain-scissions at doses bellow 250 kGy [5].

The most important factor of solid-state morphology that affects the rate of degradation of solid polymers (fibers or films) is crystallinity [6]. Fig. 4 shows crystallinity values of PCL, PLLA and PLLA normalized crystallinity in the blends as a function of radiation dose. The normalized crystallinity of PLLA all blends have the same behavior at each dose up to 75 kGy, above this dose it is observed a small decrease of the crystallinity. PCL crystallinity of the blends were not calculated because they are influenced by the glass transition of PLLA. PCL homopolymer crystallinity is not significantly affected by radiation dose in the range studied, as well.

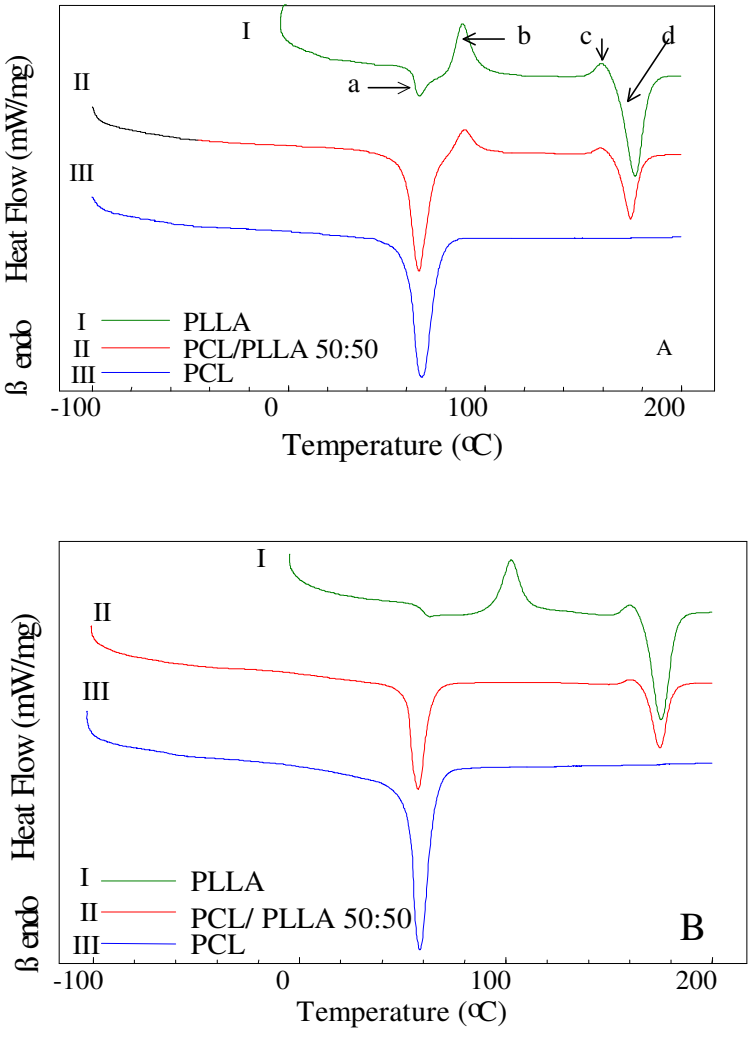

Figure 2. DSC curves from PLLA, PCL and PCL:PLLA 50:50 non-irradiated blends. (A) first heating and (B) second heating.

Despite of the difficulty on visualizing PCL glass transition in DSC curves, due to its poor resolution, shown in Fig. 2 and 3, Tg values of this component in the blends are in the range of –60 to –66 ^{o}C, independently on the blend composition and radiation dose applied.

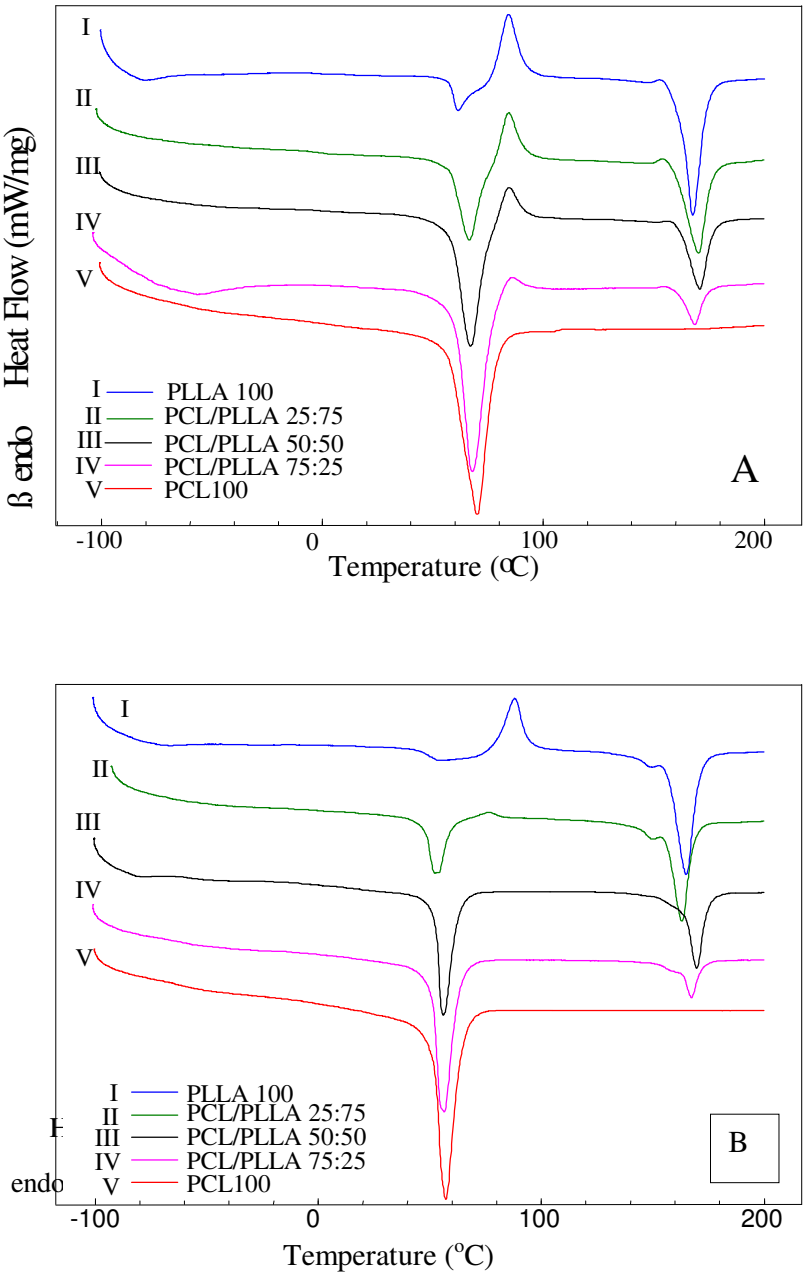

Figure 3. DSC curves from PLLA, PCL and PCL:PLLA 50:50 irradiated with 100 kGy radiation dose. (A) first heating and (B) second heating.

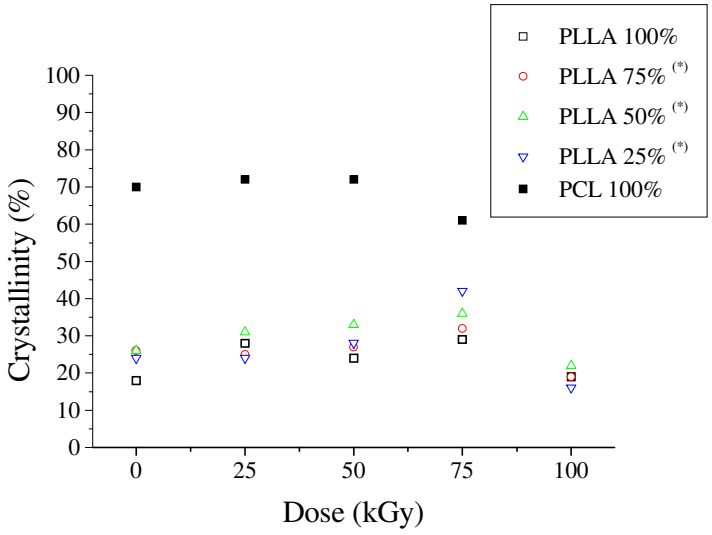

Figure 4. Normalized crystallinity versus irradiation dose.
(*) crystallinity from melting peak of PLLA component in DSC curve of blends.

3. CONCLUSIONS

Gamma radiation does not affect significantly thermal properties of the studied blends when doses were kept bellow 75 kGy. As it could be observed by the results, the sterilization by gamma irradiation does not affect thermal properties of the studied blends.

PLLA probably undergoes main chain-scissions at dose range studied. This process may led to a small decrease of PLLA T_m. 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 are not significantly affected by irradiation at the dose range studied.

In order to identify the predominant effect of the gamma radiation– crosslinking or main chain scission – on the blends during sterilization process, other analytical techniques, such as thermogravimetry, mechanical tests, FTIR would help to observe if some degradation of the blends occurs due to irradiation process.

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