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EFFECT OF STERILIZATION DOSE ON ELECTRON BEAM IRRADIATED BIODEGRADABLE POLYMERS AND COCONUT FIBER BASED COMPOSITES

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ABSTRACT

In Brazil, annual production of coconut fruit is 1.5 billion in a cultivated area of 2.7 million ha. Coconut fiber applications as reinforcement for polymer composites, besides reducing the coconut waste, would reduce cost of the composite. On the other hand, biodegradable polymers have been receiving much attention due to the plastic waste problem. Poly(ε-caprolactone), PCL, and poly(lactic acid), PLA, besides being biodegradable aliphatic polyesters, are biocompatible polymers. Considering the biomedical application of PLA and PCL, their products must be sterilized for use, and ionizing radiation has been widely used for medical devices sterilization. It is important to study the effect of ionizing radiation on the blends and composites due to the fact that they are based on biocompatible polymers. Is this research, hot pressed samples based on PLA:PCL (80:20, ratio of weight:weight) blend and the composites containing chemically treated or untreated coconut fiber (5, 10%) were irradiated by electron beams and gamma radiation from Co-60 source at doses in the range up to 200 kGy. Thermal mechanical analysis (TMA) and gel fraction measurements were performed in irradiated samples. From TMA curves it can be observed that thermal stability of samples with untreated coconut fiber slightly decreased with increasing fiber content. On the other hand, deformation increased with increasing fiber content. Acetylated coconut fibers slightly decreased thermal stability of samples. It seems that no interaction occurs between the natural fibers and the polymeric matrix due to irradiation. PLLA undergoes to main chain scission under ionizing irradiation according to thermal stability results and also because no gel fraction was observed. In contrast, PCL cross-linking is induced by ionizing radiation that increases thermal stability and decreases deformation.

1. INTRODUCTION

Biodegradable polymers have been receiving much attention due to the plastic waste problem. Poly(ε-caprolactone), PCL, and poly(lactic acid), PLA, besides being biodegradable aliphatic polyesters, are biocompatible polymers [1]. In Brazil the annual production of coconut fruit is 1.5 billion in a cultivated area of 2.7 million ha, 140 coconut fruit/tree [2]. Coconut husk has been used for just some few applications, for instance, cushion reinforcement, vases and some house tapestry, among others. The use of vegetable fibers as reinforcement for polymer composites has been growing. In the research field of coconut fiber new applications, besides reducing the waste, would reduce cost of the composite and furthermore, would act as a social project, by increasing jobs for local population of coconut products manufacturer or coconut juice consumption [3]. Considering the biomedical application, the products must be sterilized for their use, and ionizing radiation has been widely used for medical devices sterilization. The blends and composites studied here are based on biocompatible polymers, so it is important to study the effect of ionizing radiation on those materials. Is this study, hot pressed samples based on PLA, PCL, their 20:80 (w:w) blend and composites containing untreated and chemically treated coconut fiber (5 and 10%) were prepared at National Institute of Advanced Industrial Science and Technology, AIST. Sheets were irradiated using gamma radiation from Co-60 source and electron beam (EB) from electron accelerator using doses from 0 to 200 kGy at Japan Atomic Energy Agency, JAEA. The effect of ionizing radiation dose was studied by Thermomechanical Analysis, TMA, and Gel fraction measurements of the samples.

2. MATERIALS AND METHODS

2.1. Sample Preparation

PCL (pellets, $\overline{M}_W$=2.14·10^5 g·mol^{-1}; $\overline{M}_W / \overline{M}_n$ = 1.423), PLLA (pellets, M_w=2.64·10^5 g·mol^{-1} $\overline{M}_W / \overline{M}_n$ = 1.518 – Gel Permeation Chromatographic values) and dry coconut fiber (from *Embrapa – Empresa Brasileira de Pesquisa Agropecuária*) were used to prepare blends and composites. A Labo Plastomil, model 50C 150 of Toyoseiki twin screw extruder was used for pellets preparation. Pellets of PLLA:PCL 80:20 (w:w) blend and composites containing untreated and chemically treated coconut fiber (5 and 10%) were prepared at AIST. The subsequent processing and measurements presented in this study were performed at JAEA.

2.1.1. Hot pressed sheets

Sheets (150mm x 150mm x 0.5mm) of PCL, PLLA, PLLA:PCL 80:20 (w:w) blend and composites containing untreated and chemically treated coconut fiber (5 and 10%) were prepared using Ikeda hot press equipment. Mixed pellets of samples were preheated at 195°C for 3 min and then pressed by heating at the same temperature for another 3 min under pressure of 150 kgf·cm^{-2}. The sample was then cooled by cold press using water as a coolant for 3 min.

2.2. Irradiation

Hot pressed samples were irradiated in nylon/polyethylene bags sealed after removal of the air by a vacuum pump. The sheets were irradiated by electron beam from an accelerator with beam energy of 2 MeV and current of 2 mA, at a dose rate of·10 kGy·pass^{-1} with radiation doses up to 200 kGy. Samples were also irradiated by gamma radiation from Co-60 source at a dose rate of 10 kGy·h^{-1}.

2.3. Thermomechanical Analysis, TMA

Non-irradiated and EB irradiated 0.5mm thick film samples were cut into 5mm x 20mm from hot pressed sheets. For each sample it was measured width and thickness in 3 different points and it was considered the average for cross sectional area calculation. It was utilized TMA 60 WS of Shimadzu Co. Test was performed using extension probe, load of 2.5 g; from room temperature up to 200°C, heating rate 10°C·min^{-1}. Measurements were performed in nitrogen atmosphere, gas flow 50 mL·min^{-1}.

2.4. Gel-sol fraction

Samples of around 20mg were weighted in triplicate. The gel content of the cross-linked samples was estimated by measuring their insoluble part after immersion in chloroform for 48 h at room temperature. Gel formed was vacuum dried at 50°C for 24 h.
The gel fraction was calculated using Eq. 1:

$$\text{Gel Fraction } (\%) = \frac{W_i}{W_f} \cdot 100 \quad . \tag{1}$$

where W_i is the initial weight of the dried sample after irradiation, and W_f is the weight of the dried insoluble part of sample after extraction with chloroform.

3. RESULTS AND DISCUSSION

PLLA:PCL blends present poor mechanical properties due to the macro-phase separation of the two immiscible components and the poor adhesion between the phases. Processing conditions and a variety of parameters of the polymeric components determine the distribution of the dispersed phase that affects the morphology and consequently the mechanical properties of blends [1].

Information about the actual phase of the specimen, including its thermal and mechanical history can be obtained from the first heating phase. When thermoplastics soften, especially above glass transition, orientations and stresses may relax, as a result of which post-crystallization and recrystallization processes may occur. On the other hand the specimen may deform under the applied test load. [4].

Fig. 1, 2 and 3 present the radiation dose effect on thermal stability of PCL, PLLA and PCL:PLLA 20:80 (w:w) blend studied by TMA.

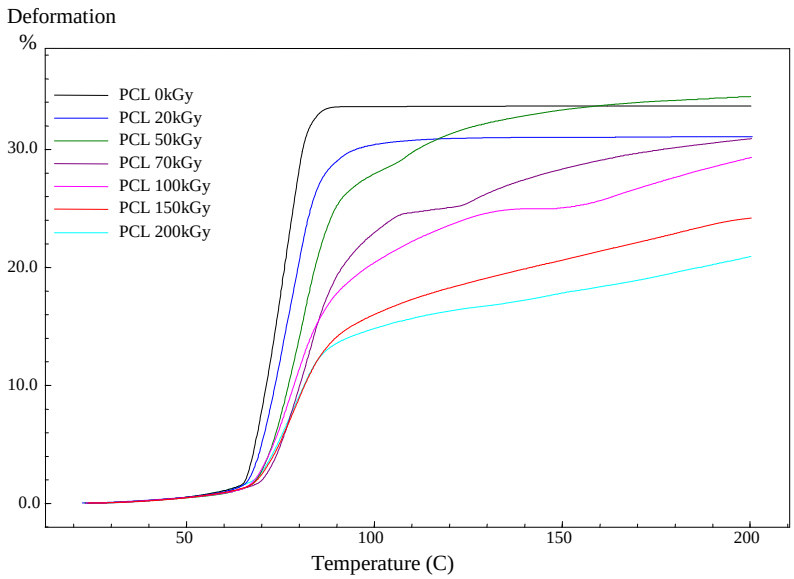

Figure 1. TMA curves of EB-irradiated PCL samples up to doses of I) 0 kGy, II) 10 kGy, III) 20 kGy, IV) 50 kGy, V) 100 kGy, VI) 180 kGy and VII) 200 kGy.

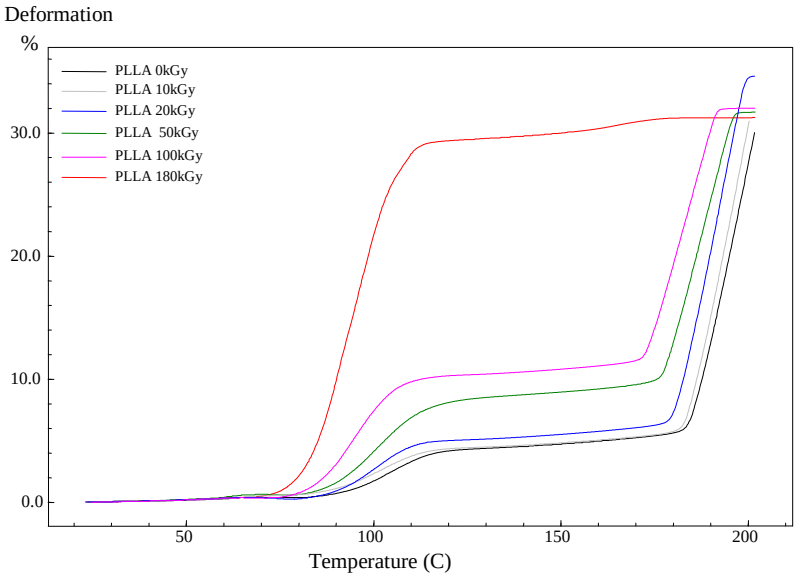

Figure 2. TMA curves of EB-irradiated PLLA samples up to doses of I) 0 kGy, II) 10 kGy, III) 20 kGy, IV) 50 kGy, V) 100 kGy, VI) 180 kGy and VII) 200 kGy.

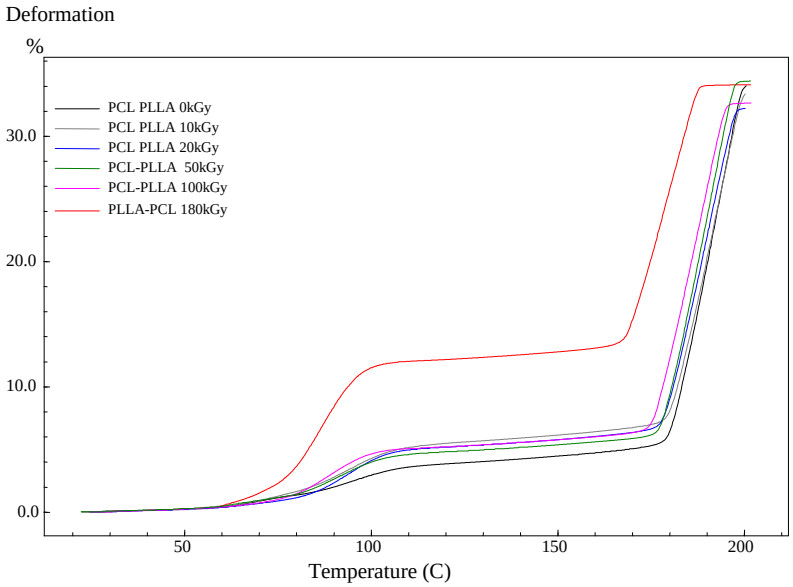

Figure 3. TMA curves of EB-irradiated PCL:PLLA (20:80) samples up to doses of I) 0 kGy, II) 10 kGy, III) 20 kGy, IV) 50 kGy, V) 100 kGy, VI) 180 kGy and VII) 200 kGy.

Crystals of rigid macromolecules show no known equilibrium effects of mechanical deformation on melting transitions, since their melts cannot maintain a tensile stress under equilibrium conditions. In a network of molten, flexible molecules, a state of stress can be maintained indefinitely given the proper boundary conditions of strain. Even if the molecules are not permanently linked through covalent cross links, entanglements or crystals connecting portions of molecules may set up a network for a sufficiently long time to change the melting point. When held at constant length the force must increase on melting, raising the melting temperature of the remaining crystals [5].

In this study, non-irradiated PCL samples start to deform in the range of 65 to 90°C due to melting, as it can be observed in Fig. 1. By increasing radiation dose, thermal stability of the studied samples is slightly enhanced although the deformation under load decreases as a function of temperature.

PCL samples submitted to absorbed EB radiation doses of 20 kGy, 50 kGy and 100 kGy have shown a second step of deformation under load probably due to the start of cross-linked gel fraction formation. This behavior is not observed for non-irradiated sample as well as for those submitted to higher radiation doses such as 180 kGy and 200 kGy. The higher doses are able to enhance the degree of cross-linking and consequently gel fraction, which seems to be responsible for the melting temperature increase and lower total deformation of PCL samples under the same load.

When the PLLA is exposed to a gamma-ray or an electron beam, the mechanical and physical properties of the polymer decrease due to reduction of the molecular weight of the polymer [6]. In this study, it was observed that non-irradiated PLLA samples start to deform at 75°C when submitted to constant extension load. This deformation can be associated to the glass

transition. A second step of deformation can be observed at around 180°C, which is attributed to the melting process. Fig. 2 shows that raising radiation doses the deformation increases meanwhile the thermal stability of PLLA decreases. PLLA samples irradiated with 180 kGy present just one step of deformation, suggesting that PLLA undergoes predominantly degradation as observed previously [6].

TMA curves in Fig. 3 show that the presence of PCL on PCL:PLLA 20:80 (w:w) blend affects somewhat the thermal stability of PLLA in irradiated samples. Moreover, the decrease on the glass transition temperature of PLLA, PCL also induces decreasing in the measured deformation (%) of the first step of the TMA curves, attributed to PLLA glass transition, mainly for samples submitted to higher doses such as 180 kGy probably because of PCL cross-linking. In the dose range studied it is possible to observe two steps of deformation for all doses.

Dose effects on thermal stability of composites with 5% and 10% untreated and acetylated coconut fiber studied by TMA can be observed on Fig. 4 up to Fig. 7.

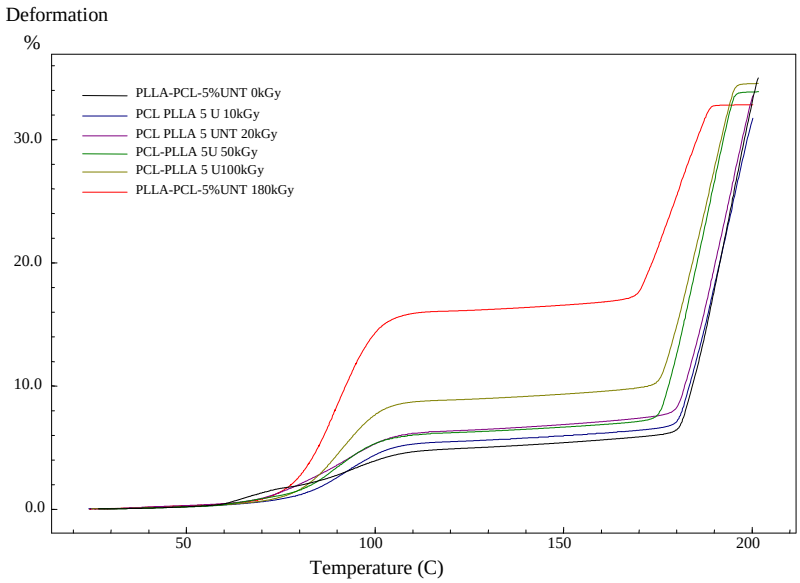

Figure 4. TMA curves of PCL:PLLA (20:80) with 5% of untreated coconut fiber, EB-irradiated up to 180 kGy radiation dose

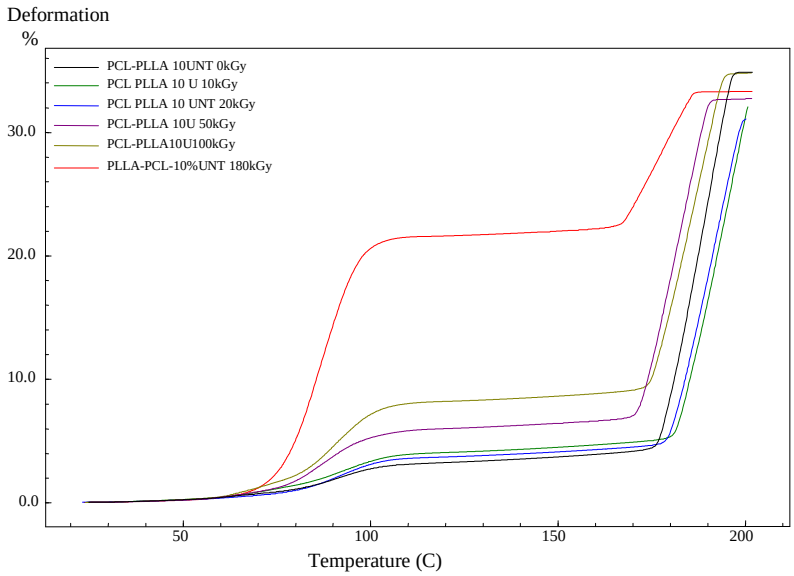

Figure 5. TMA curves of PCL:PLLA (20:80) with 10 % of untreated coconut fiber, EB-irradiated up to 180 kGy radiation dose

Thermal stability of samples with untreated coconut fiber slightly decreased with increasing fiber content. On the other hand, deformation increased with fiber increase, as observed in Fig. 4 and Fig. 5 compared to Fig. 3. Deformation increased with radiation dose for all composites.

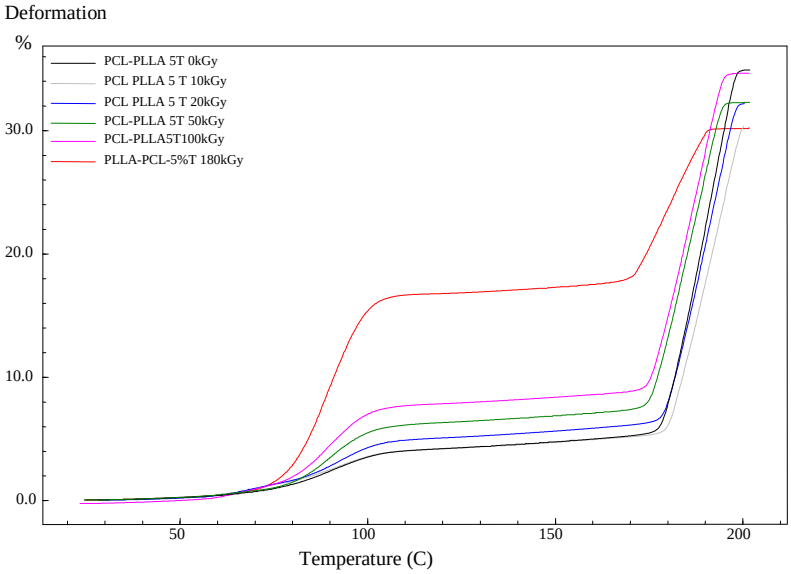

Figure 6. TMA curves of PCL:PLLA (20:80) with 5% acetylated coconut fiber EB-irradiated up to 180 kGy radiation dose.

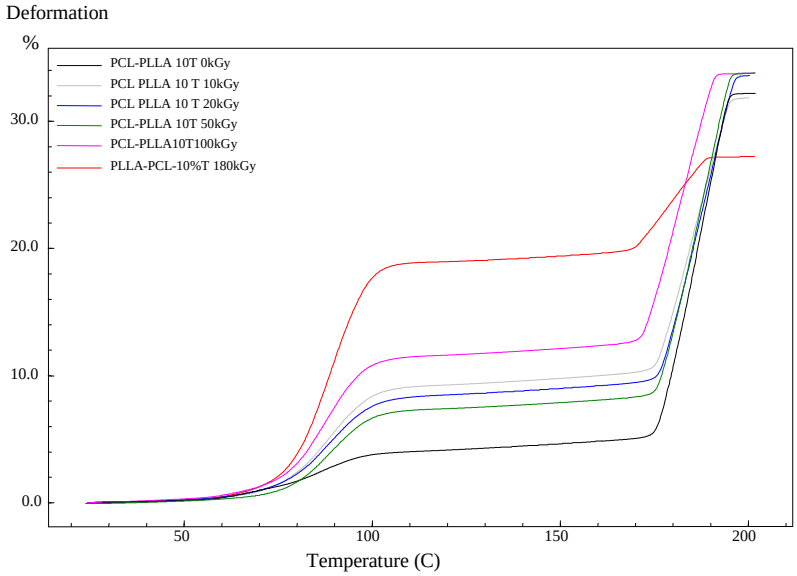

Figure 7. TMA curves of PCL:PLLA (20:80) with 10% acetylated coconut fiber EB-irradiated up to 180 kGy radiation dose.

Acetylated coconut fibers slightly decreased thermal stability of samples as observed in Fig. 6 compared to Fig. 3, Fig 4 and Fig. 5. Deformation of acetylated coconut fibers composites increased with increasing fiber content. Furthermore, deformation increased with increasing PLLA glass transition and PCL melting processes, and the second step of deformation is due to PLLA melting.

When polymers that predominantly crosslink under ionizing radiation, chemical bridges are formed between adjacent molecules which become permanently linked. This may result in significant properties alteration as mechanical behavior, solubility and swelling. In a wide range of doses, the number of such bonds is assumed to be proportional to the absorbed dose. Gel sol fraction analysis of irradiated polymers allow to estimate important parameters of radiation effect as cross-linking and degradation, gels dose, and correlate them to some physicochemical properties [7].

It can be observed in Table 1 that gel fraction starts to present measurable values above 100 kGy for both PCL gamma and EB irradiated samples. PLLA and PCL:PLLA 20:80 blend do not present gel fraction values, even though it has been possible to visualize some fragile gel portion on the blends irradiated above 100 kGy. It can be suggested that PLLA predominantly does not crosslink in the dose range studied. Furthermore, comparing gamma radiation and EB allow verifying that radiation dose rates do not affect the gel formation. Also for the composites irradiated with doses above 100 kGy it was possible to observe a gel like formation. It seems that fiber presence does not affect gel formation. In addition it looks as if no interaction occurs between fiber and polymeric phase, because fibers were dispersed in the solvent during measurements.

Table 1. Dose effect on gel fraction of PCL

Dose (kGy)	Gel Fraction (%)	
	Gamma	EB
0 – 70	Not detected	Not detected
100	30	-
150	-	40
160	45	-
200	49	47

From the results of gel fraction measurements it can be observed that EB irradiated PCL presents 40% of gel fraction when submitted to 150 kGy of absorbed radiation dose. Even though, PCL gel formation has been observed, no gel formation was detected for PLLA, in the dose range studied. This fact suggests that irradiated PLLA undergoes predominantly to scission. For the blends and composites of all concentrations of chemically treated and untreated coconut fiber, just a very small quantity of a gel like substance was observed as a circular line in the internal wall of the vials containing the samples irradiated with doses higher than 150 kGy. This looks like the PCL fraction undergoes some cross-linking reaction even being dispersed into the PLLA matrix. The coconut fibres of the composites were released from the polymeric matrix for all samples during the gel fraction analysis. It seems that no interaction occurs between the natural fibres and the polymeric matrix due to irradiation. Only for PLLA homopolymer hot pressed plates preparation it was observed some bubbles, which suggests that PLLA is very sensible to thermal processing.

4. CONCLUSIONS

In this study, PLLA undergoes to main chain scission under ionizing irradiation according to thermal stability results and absence of gel content. In contrast, PCL cross-linking is induced by ionizing radiation that increases thermal stability and decreases deformation. Furthermore, gel fraction is observed at doses above 100 kGy. PCL presence affects PLLA thermomechanical behavior in the blend. Coconut fiber presence slightly affects thermal stability and deformation with its increasing content and radiation doses. It seems that no interaction occurs between the natural fibres and the polymeric matrix due to irradiation. To improve this study, thermal and mechanical properties of those composites have been studied and the results will be analyzed and the final results will be presented in future works.

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