1. Introduction

The problem of non-biodegradable plastic waste remains a challenge due to its negative environmental impact. In this sense, 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 [1-5]. PLLA is a poly(α-hydroxy acid) and PCL is a poly(ω-hydroxy acid) [1]. PLLA is a hard, transparent and crystalline polymer. 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 [6]. The original reasons for preparing polymer blends are to reduce costs by combining high-quality polymers with cheaper materials (although this approach is usually accompanied by a drastic worsening of the properties of the polymer) and to create a polymer that has a desired combination of the different properties of its components. However, according to Michler [7] usually different polymers are incompatible. Improved properties can be only realized if the blend exhibits optimum morphology. According to Sawyer et al. [8], in polymer science, the term morphology generally refers to form and organization on a size scale above the atomic arrangement, but smaller than the size and shape of the whole sample. Thus, improving compatibility between the different polymers and optimizing the morphology are the main issues to address when producing polymer blends [3]. Moreover, both polymers PLLA and PCL can be used in biomedical applications, which require a proper sterilization process. Nowadays, the most suitable sterilization method is high energy irradiation. However, it is important to remind that polymeric structural changes are induced by radiation processing of polymers, such as scission and crosslinking [9-12]. According to the principles of radiation chemistry, very reactive intermediate, free radicals, ions and excited states are formed when...
macromolecules of polymers are submitted to ionizing radiation, where they are then free to react with one another or initiate further reactions among the polymeric chains, thus giving rise to changes in material properties. These intermediates can follow several reactions paths that result in disproportion, hydrogen abstraction, arrangements and/or formation of new bonds. The combination of two radicals leads to cross-linking or recombination in the amorphous and crystalline regions, respectively, whereas chain transfer and the subsequent splitting results in chain scission. Usually both these processes take place simultaneously for many polymers [10,11].

The morphology of the blends affects the thermo mechanical properties as well as the biodegradation of the polymers. In particular, surface structure and morphology of the biodegradable polymer blends have a great impact on the enzymatic degradation behavior. The development of polymeric materials susceptible to microbiological degradation and that have similar performance to conventional polymers has been intensely studied. The intention would be that those materials reduce waste volume while suffer degradation in sanitary waste deposit, or they could be treated in composting plants [13]. Enzymatic and non-enzymatic degradations occur easier in the amorphous region [14,15]. Kikkawa et al. [16] cited that one of the approaches used to generate biodegradable materials with a wide range of physical properties is blending, and miscibility of blends is one of the most important factors affecting the final polymer properties.

Nishino et al. [17] cited that cellulose is the most abundant form of biomass and the form most likely to be used as reinforcement fibers, not only because of ecological and economic reasons, but also because of their high mechanical and thermal performance. Thus, incorporating fibers of low cost to the polymeric blend, it is possible to obtain an improvement of the mechanical properties without loss of the original characteristics of polymeric components. Regarding the irradiation effects, vegetable fiber, like as coconut fiber, is composed by cellulose and lignin, which suffer chemical alteration by irradiation such as scission or cross-linking. In the case of natural polymers, such as cellulose, main chain scission occurs predominantly due to irradiation and as a result molecular weight’ decrease [10].

Liu et al. and Lenglet et al. [18,19] cited that biodegradability of PCL and PLLA has also been investigated under environmental conditions. The controlled degradation of polymers is sometimes desired for biomedical applications, besides the environmental purposes [7]. It has been seen that PLLA is bio absorbable, that is, the hydrolytic degradation by-products formed can be fully assimilated by microorganisms such as fungi or bacteria. On the other hand, PCL is promptly biodegraded by environmental microorganisms. So, both PCL and PLLA can be considered as environmentally friendly polymers.

Kolybaba et al. [20] mentioned that biodegradable plastics are those that undergo significant enough modification on their chemical structure under specific environmental condition. Those changes result on mechanical and physical properties losses that are measurable by standard methods of testing. Biodegradable plastics suffer degradation under action of microorganisms that has natural occurrence, for instance, bacteria, fungi and algae. The plastic engineered to be entirely biodegradable is classified within the main classes of polymeric materials. In this category, polymeric matrix can be from natural resources and reinforcement
fibers would be obtained from vegetal fibers. So, microorganisms are able to consume completely those materials, eventually releasing carbon dioxide and water as by-products [20]. PCL, PLLA and coconut fiber composites studied in this chapter may be categorized in that class.

According to Müller [13], there are different approaches concerning the type of test to be applied to evaluate degradation of polymeric materials in the environment and, also, what conclusion can be obtained from that. As principle, tests can be divided in three categories, field test, simulation and laboratorial tests. Nevertheless field test, for instance, in which samples are buried on the ground, or putting them in a lake or river, or performing general process of composting of polymeric biodegradable material, represent the ideal practical conditions. There are several disadvantages associated to this kind of test. One of the problems would be to control environment conditions like temperature, pH, or humidity. Another point to be considered is to analytically monitor the degradation process, in most cases it would be possible to visually evaluate alterations of the sample, or maybe evaluate the disintegration by measuring weight loss. Most reproducible tests are laboratorial ones, well-defined medium and, inoculated with specific microorganisms to a particular polymer are utilized. In those cases, enzymatic activity is optimized to a particular microorganism and, frequently present more elevated degradation rate than the ones observed in natural conditions. This is considered as an advantage to the study of basic mechanism of polymer biodegradation. Although results lead to limited conclusion related to real degradation rate on the natural environment, those tests have widely been used.

2. Material and method

2.1. Material

Samples of PCL and PLLA homopolymers; PCL:PLLA 20:80 (w:w) blend; and composites of the blend containing 5% and 10% of coconut fiber (chemically untreated and acetylated) were prepared in triplicate.

2.2. Coconut fiber

Coir coconut fibers for composite preparation were kindly provided by Embrapa – Paraipaba region, Ceará.

Size reduction of the coconut fibers was carried out using helix mill Marconi – modelo MA 680, from Laboratório de Matéria-prima Particulados e Sólidos Não Metálicos – LMPSol, Departamento de Engenharia de Materiais de Escola Politécnica/USP.

The fiber size distribution was measured using sieves of the Tyler series 16, 20, 35 and 48, fiber sizes of 1.0mm, 0.84mm, 0.417mm, and 0.297mm, respectively. The 0.297-0.417mm fibers size was used for the assays. The triturated material was separated using a sieve shaker Produtest, for 1 min.
In order to remove lignin from coconut fiber surface, fibers were soaked with Na$_2$SO$_3$ 2% aqueous solution for 2h using ultrasound. Coconut fibers were washed several times with tap water and finally, three times with deionized water, as described in the literature [21].

Coconut fiber acetylation was performed as described by d’Almeida et al. [22]. As received fibers from Embrapa were soaked in a solution of acetic anhydride and acetic acid (1.5:1.0, w:w). It was used as a catalyst, 20 drops of sulfuric acid in 500mL solution. Those groups of sets were submitted to ultrasound for 3h, then for more 24h rest at the same solution. Fibers were washed using tap water and for more 24h rested in deionized water. Fibers were separated from water and washed with acetone, after that, were evaporated at room temperature.

2.3. Preparation of composite pellets and sheets

PCL (pellets, $\bar{M}_w = 2.14 \times 10^5$ g·mol$^{-1}$; $\bar{M}_w / \bar{M}_n = 1.423$), PLLA (pellets, $\bar{M}_w = 2.64 \times 10^5$ g·mol$^{-1}$ $\bar{M}_w / \bar{M}_n = 1.518$ – Gel Permeation Chromatographic values) and dried coconut fiber (from Embrapa – Empresa Brasileira de Pesquisa Agropecuária, Ceará, Brazil) 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 PCL:PLLA 20:80 (w:w) blend and composites containing 5 and 10% of untreated and chemically treated coconut fiber were prepared at AIST.

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

For degradability tests, samples were taken from hot compressed polymeric sheets, cut into 15mm × 15mm pieces. Non-irradiated and, electron beam (EB), irradiated samples with absorbed doses of 50 kGy and 100 kGy were studied.

2.4. Electron beam irradiation

Irradiation was performed at JAEA using electron beam accelerator (2 MeV; 2 mA), absorbed doses of 50 and 100 kGy, dose rate of 0.6 kGy s$^{-1}$. The energy and current parameters condition of irradiation were enough to the electron beam goes through the 0.5mm thickness sheets.

Absorbed dose is the amount of energy absorbed per unit mass of irradiated material. The SI unit for absorbed dose is joules per kilogram (J kg$^{-1}$), which is given the special name gray (symbol, Gy). The absorbed dose rate is the absorbed dose per unit time and has the units gray per unit time, for instance kGy s$^{-1}$. The absorbed dose is a direct measure of the energy transferred to the irradiated material that is capable of producing chemical or physical change [23].
3. Method

3.1. Enzymatic degradation

A buffer solution with phosphate, pH 7, and lipase enzyme obtained from *Pseudomonas cepacia*, of Aldrich, was prepared. Solution concentrations were kept at 35 unities of enzymatic activity. Flasks were maintained in hot water bath at 37°C. System buffer-enzyme was preserved by 7 days (168h). Samples were exposed to enzymatic action for 0, 24, 72, 120 and 168 hours. After enzymatic exposure, samples were washed with water, dried and weighted (mass retention determination). Tests were performed in duplicate, subtracted test control without enzyme.

3.2. Biodegradability in soil

Samples of approximately 10mm × 10mm were buried in plastic trays containing simulated compost soil previously prepared, with 23 % humus, 23 % organic material (tree leaves, coffee powder, food waste and cattle manure), 23 % sand and distilled water to complete 100 %. Simulated compost was characterized for nitrogen and total carbon content, ABNT 1167 and, pH. Simulated compost soil characterization results: pH 7.8; humidity 30 ± 10 %; total carbon 18.4 %; total nitrogen 0.83 %. Samples were removed from the soil at 30, 60, 90 e 120 days of ageing. After that, they were mechanically cleaned, and dried at room temperature for 24 hours.

4. Results and discussion

4.1. Enzymatic degradation

Enzymatic degradation was performed using lipase enzyme obtained from *Pseudomonas cepacia*. In Fig. 1 it can be observed mass retention variation of non-irradiated and electron beam (EB) irradiated samples through time of degradation of homopolymers, blend and composites. Degradation rate of PCL is higher than PLLA in *Pseudomonas* lipase presence, in agreement with observed by Liu et al. [18] that lipase degrade both crystalline and amorphous PCL. According to Liu et al., enzymatic degradation of PCL has been investigated, mainly in presence of lipase enzyme. It is well known that morphology and its alteration plays an important role on hydrolytic degradability of aliphatic polyesters [18]. When the subject is enzymatic degradation, situation complicates due to specificity of enzymes. *Pseudomonas* lipase is able to break esters linkages in hydrophobic substrates, as it is PCL case. Also, it was described that PCL did not absorb water, by the other side, PLLA absorbed 2% water within 72h. The authors also informed that degradation rate of this polymer is higher in proteinase K than in lipase (8% against 1%). However, in the study of this chapter it was observed that PCL degraded approximately 30%, and PLLA 16%, at the same period of time. According to Tsuji and Ishizaka, no alteration was observed on the molar weight distribution, either mass loss of pure PLLA studied films, indicating that enzymatic hydrolysis effect caused by *Pseudomonas*
lipase on the main chain of PLLA on the bulk was not significant. This confirms that enzymatic degradation occurs preferably on the surface of the sample [15].

Calil et al. and Sivalingam et al. [24,25] cited that the presence of one polymer affects degradability of the other polymer. Lenglet et al. observed that PLLA addition to PCL reduced drastically degradation of PCL of the blends in lipase presence [19]. In the study presented in this chapter, it was possible to observe that the presence of PLLA reduced enzymatic degradation of PCL of PCL:PLLA 20:80 (w:w) blend, and after 120 hours, mass retention variation moved toward of pure PLLA behavior. Tsuji and Ishizaka [15] studied enzymatic degradation of PCL:PLLA blends using *Rhizopus arrhizus* lipase. They observed that enzymes obtained from fungi cause selective hydrolysis and PCL removal of PCL:PLLA blends without significant PLLA degradation in soil. They also cited that enzymatic degradation of PCL:PLLA in presence of *Pseudomonas* lipase and Proteinase K occurred in the interface of two polymeric phases both on the bulk and on the surface of the sample.

![Figure 1](image-url)

**Figure 1.** Mass retention variation versus degradation time, enzymatic method, of samples: (■) PCL; (●) PLLA; (▴) PCL:PLLA 20:80 (w:w); (□) composite with 5% of untreated fiber; (◇) composite with 10% of untreated fiber; (◁) composite with 5% of acetylated fiber; and (○) composite with 10% of acetylated fiber, of non-irradiated samples.

In the study of this chapter, composites degraded in a way similar of the blend through time. Mass retention values observed were higher than the blends during the same period of time of test, suggesting that coconut fibers did not significantly enzymatic degraded in this test condition. Furthermore, acetylation did not affect enzymatic degradation of composites significantly.

Tsuji and Ishizaka [15] observed that crystallinity of PCL on blends films did not change with composition variation during degradation, suggesting that this property did not affect enzymatic hydrolysis rate of PCL of the blend as it did not altered during process. Rate of enzymatic hydrolysis of blends was lower than pure PCL, suggesting that PLLA interfered on PCL hydrolysis catalyzed by lipase. One reason postulated by the authors to the deceleration
of PCL degradation on the blends would be the disturbance caused by superficial adsorption of enzyme molecules on the polymeric films or by slow hydrolytic scission of main chains of PCL by molecules enzymes on the presence of PLLA molecules on the blends.

Fig. 2 shows points of lipase enzyme attack on polyesters proposed by [25].

![Figure 2. Points of enzyme attack on polyesters by lipase: a) PLA; b) PCL; c) PCL:PLA 14:86 (extracted from Sivalingam et al. [25])](image)

On Fig. 3 it is possible to observe effect of radiation dose on enzymatic degradation of PCL samples irradiated with electron beam.

According to Cottam et al. [26], degradability rate of PCL irradiated with 25 kGy decreased, attributed to irradiation process. Authors cited that lipase catalyzes hydrolysis of carbonyl group linkage and one oxygen atom in the case of fat. It is the same linkage that is broken during PCL hydrolysis. They attributed that degradability rate of PCL was affected by crosslinking occurred due to irradiation. In this study, PCL irradiated with 50 kGy suffered a slight decrease on degradation rate, in agreement with authors’ observation. However, PCL samples irradiated with 100 kGy presented a certain increase on degradation rate. This fact probably is related to crystallinity decrease of around 6% observed by Differential Scanning Calorimetry, DSC, of irradiated samples. On Fig. 4 it is possible to observe the effect of radiation dose on enzymatic degradation of PLLA samples irradiated with electron beam.

According to Maharana et al. [27], enzymatic degradation occurs only on the surface of a solid substrate by erosion on the surface and by weight loss, because enzymes cannot penetrate a solid polymeric substrate. Enzymes degrade selectively amorphous regions or less ordered that allows them to diffuse through substrate and, subsequently, crystalline regions are eventually degraded. In this process, molar weight and molar weight distribution of non-degraded solid substrate do not change during enzymatic degradation because only the polymer on the surface of substrate is degraded and products of low molar weight from degradation are removed of substrate by solubilization on the surrounding aqueous medium.
There are two kinds of degradation based on the point of cleavage. Cleavage can occur in random points along polymeric chain (degradation endo-type) or at the end terminal of main chain (degradation exo type). Degradation process of lipases is based on endo type scission, so it does not depend on molar weight and on molar weight distribution. Fig. 5 shows PLA hydrolysis reaction cited by [27].
Figure 5. Hydrolysis of PLA [27].

On Fig. 6 it can be observed mass retention variation through period of enzymatic degradation of PCL:PLLA 20:80 (w:w) non-irradiated and irradiated with electron beam with absorbed radiation doses of 50 kGy and 100 kGy. Degradation values observed in this study were lower compared to the ones found in the literature, probably due to the fact that studied samples were physical mixtures of polymers. Lenglet et al. [19] studied enzymatic degradation of PCL:PLLA copolymers with $M_n$ of 29,000 to 44,000, using Pseudomonas lipase. Authors observed that degradation occurred faster with increasing amount of PCL, attaining approximately 99% for PCL:PLA 75:25 after 72h. They suggested that PCL homopolymer can suffer degradation in presence of Pseudomonas lipase while PLA did not degrade in the same conditions.

In Fig. 6 irradiated blend with absorbed dose of 50 kGy presented slight reduction of degradation rate compared to non-irradiated blend, similar to the observed for homopolymers. Irradiated sample with 100 kGy showed slight increase of degradation rate after 120 hours, and then, little degradation is observed.

In Fig. 7 it is shown mass retention variation versus degradation period, by enzymatic method, of composites with 5% of chemically untreated coconut fiber, non-irradiated and EB irradiated with absorbed doses of 50 kGy and 100 kGy.

Chemically untreated fiber incorporation caused slight reduction of degradation comparing blend to composite. Probably, it is due to the fact that fibers take more time to degrade. Even though the method used by Salazar and Leão [28] was different from the one used in this study, they observed that fresh coconut fiber degraded 10% in 912 hours (38 days) by immediate degradability test, by measuring carbon dioxide release in open system, in which organic substance is subjected to metabolizing of microorganism mixture culture from environment. This carbon source of the substance can be fully consumed by microorganism metabolism into CO$_2$ and H$_2$O. It is possible to predict theoretically total CO$_2$ production for full biodegradation, knowing initial carbon content.
Figure 6. Mass retention variation with period of degradation, enzymatic method, of PCL:PLLA 20:80 (w:w) non-irradiated and EB irradiated samples with 50 kGy and 100 kGy absorbed doses.

Figure 7. Mass retention variation versus degradation period, enzymatic method, composites with 5% of chemically untreated coconut fiber, non-irradiated and EB irradiated with absorbed doses of 50 kGy and 100 kGy.

In Fig. 7 it is observed that degradation rate of composites behaves in a way similar to irradiated blends, this suggests that fiber presence does not affect this parameter. Mass retention values of samples studied in 168 hour probably were affected by water absorption by PLLA and/or coconut fibers.

In Fig. 8 it is observed that when fiber content of chemically untreated coconut fiber increases in the composite, degradation rate suffers slight reduction and degradation decreases with increasing radiation dose.
Fig. 8. Mass retention variation versus degradation period, enzymatic method, composites samples with 10% of chemically untreated coconut fiber non-irradiated and EB irradiated with absorbed doses of 50 kGy and 100 kGy.

Fig. 9 shows mass retention variation with degradation period increase, enzymatic method, of composites samples with 5% acetylated fibers non-irradiated and EB irradiated with 50 kGy and 100 kGy.

Acetylation process of coconut fiber did not affect significantly degradation rate of irradiated samples. Irradiated samples suffered slight decrease of degradation rate compared to composites containing 5% of acetylated fibers, non-irradiated.

Increase of acetylated fiber content up to 10% did not affect significantly degradation neither degradation rate of EB irradiated composites with 50 kGy and 100 kGy. It was observed slight increase on mass after 168h, probably due to water absorption by PLLA or coconut fibers, Fig. 10.

Fig. 9. Mass retention variation versus degradation period, enzymatic method, and composites samples containing 5% acetylated fiber, non-irradiated and EB irradiated with absorbed doses of 50 kGy and 100 kGy.
4.2. Biodegradation in simulated compost soil

Mass retention variation versus degradation period in simulated compost soil, of non-irradiated samples PCL, PLLA, PCL:PLLA 20:80 (w:w) blend, composites with 5% and 10% of chemically untreated fiber and composites containing 5% and 10% of acetylated fiber are shown in Fig. 11. It can be observed that all samples suffer degradation in the period of time studied. Values vary in between of 36% and 10% in 120 days for PLLA and composite with 5% of chemically untreated coconut fiber, respectively.

According to Alauzet et al. [29], PLA ester hydrolysis in abiotic aqueous media depends on autocatalysis via chain end carboxylic groups and diffusion reaction phenomena involving water and oligomer molecules formed by degradation by means of its solubility in aqueous media. When submitted to heat and water, high molecular weight PLLA degrade to oligomer (PLA of low molecular weight), dimer and monomer of lactic acid. That would explain the reason why PLA degrade in humid medium and room temperature, like organic compost or humus.

In the study of this chapter, PLLA biodegradation in simulated compost soil presented degradation rate higher than PCL, different from the behavior observed in enzymatic method, probably due to used enzyme specificity in the assay.
Figure 11. Mass retention variation versus biodegradation period in simulated compost soil, of samples: (■) PCL; (●) PLLA; (♦) PCL:PLLA 20:80 (w:w); (□) composite with 5% chemically untreated coconut fiber; (◇) composite with 10% chemically untreated coconut fiber; (◁) composite with 5% acetylated fiber; and (○) composite with 10% of acetylated fiber.

Effect of radiation dose on the mass retention of EB irradiated samples with doses of 50 kGy and 100 kGy of PCL, is presented in Fig.12; of PLLA, in Fig.13; of blend PCL:PLLA 20:80 (w:w), in Fig.14; of composite containing 5% of chemically untreated fiber, in Fig.15; of composite with 10% of chemically untreated fiber, in Fig.16; of composite with 5% of acetylated fiber, in Fig.17; and of composite with 10% of acetylated fiber, in Fig.18.

Lotto et al. [30] observed that PCL did not suffer degradation in compost soil at room temperature even after 300 days. However, after temperature increase up to 46°C, it was observed by the authors 36% weight loss of PCL samples in 120 days. This fact was attributed to non-enzymatic hydrolysis of esters bonds due to temperature increase, that condition favored microorganism action that exists in natural soil and uses polymers as nutrient.

In this study, it was observed that at room temperature PCL suffered approximately 20% of degradation in simulated compost soil in 120 days. Ionizing radiation induced degradation rate increase with increasing radiation dose in the dose range studied, Fig.12, achieving 55% of degradation in the same degradation period. Probably it was because of aerobic condition of simulated compost soil test is performed.

PLLA suffered approximately 35% of degradation in the same period as PCL, Fig.13, and irradiation process promoted degradation rate increase with increasing radiation dose, achieving 70% of degradation in 120 days.
Maharana et al. [27] cited that ionizing radiation does not affect glass transition temperature $T_g$, melting temperature $T_m$, neither hydrolytic degradation of aliphatic polyesters. However, in our study it was possible to observe slight increase of biodegradation rate in simulated compost soil after 60 days. Probably this behavior is related to microorganism presence in soil that would favor the degradation process by produced oligomer consumption. According to the authors, as radiation induced reactions occur mainly in amorphous regions of polymers, it is important to know their crystallinity degree. Biodegradation is also affected by solid state morphology, primary chemical structure, for instance, functional groups existence and hydrophicity and
hydrophobicity equilibrium of PLA. Crystallinity degree is one of the main factors that controls degradation rate of solid polymers. In general, main chain scission occurs at esters bonds sites, leading to oligomer formation, which number after chain scission depends on the quantity of ester bonds present on PLA.

Normally, biodegradation occurs in three steps. In the first step, depolymerization occurs, then, in the second step depolymerized PLA produces lactic acid. Finally, lactic acid is consumed in citric acid cycle where it is transformed into CO$_2$ and H$_2$O in the presence of an enzyme produced by microorganism. PCL:PLLA 20:80 (w:w) blend suffers degradation of approximately 30% in 120 days, PCL slightly affected PLLA degradation in the blend, Fig.14.

Radiation absorbed dose of 50kGy did not affect significant effect of degradation rate, irradiated samples with 100kGy suffered few significant increase of degradation rate after 60 days.

![Figure 14. Mass retention variation versus biodegradation period in simulated compost soil of PCL:PLLA 20:80 (w:w) non-irradiated and EB irradiated with radiation doses of 50 kGy and 100 kGy](http://dx.doi.org/10.5772/56231)

Absorbed radiation dose of 50 kGy did not significantly affect degradation of composite containing 5% of non-chemically treated coconut fiber, neither degradation rate in simulated compost soil, FIG.15. Samples irradiated with 100kGy suffered discrete increase of degradation rate after 60 days of test and over 120 days biodegradation tend to stabilize.

Absorbed radiation dose did not affect significantly biodegradation neither degradation rate of studied samples of composites containing 10% of non-chemically treated fibers, Fig.16.
It was observed during preparation of composites with acetylated coconut fibers that some kind of chemical reaction occurred during extrusion in some few events. Probably some vestiges of chemicals used for acetylation had remained on the coconut fibers. This fact could have affected degradation test of some samples of composites containing acetylated coconut fibers that started to present fissures favoring degradation on these points. Lucas et al. [31] cited that bio deterioration of thermoplastics occurs via two different mechanisms, erosion at
surface and in the bulk. In the case of bulk erosion, fragments of total mass of polymer are lost and its molecular weight is altered because of bond rupture. This rupture is provoked by chemicals (H$_2$O, acids, bases, transition metal and radicals) or by radiation, however not by enzymes. They are very big to penetrate through bulk structure. Whereas in the case of surface erosion, matter is lost, though molecular weight of polymeric matrix does not alter. If chemical substances diffusion through the material is faster than bond scission of polymer, polymer suffers erosion. If the opposite occurs, process occurs mainly on the surface of polymeric matrix.

Radiation dose did not affect significantly biodegradation of composites containing 5% of acetylated fibers up to 60 days of test. Irradiated samples with 100kGy presented slight increase on the degradation rate after 90 days, Fig. 17.

On Fig. 18 it is possible to observe that composites samples containing 10% of acetylated fiber did not suffer significant alteration of degradation rate with radiation dose increase.

![Figure 17. Mass retention variation versus period of biodegradation in simulated compost soil of composites samples containing 5% of acetylated fibers, non-irradiated and EB irradiated with absorbed doses of 50 kGy and 100 kGy](http://dx.doi.org/10.5772/56231)

Higher degradation values found of those samples compared to non-chemically treated fibers could be related to the effect of fissures observed on the polymeric matrix during test that probably favored microbiological attack.

Mass retention results deviations were in average 7%, probably due to weight variation of sample to sample.
4.3. Hydrolytic degradation

This section will present some aspects of hydrolytic degradation because PCL and PLLA homopolymers studied here are biomaterials.

Biodegradability of polymeric materials occurs in several steps. Initially, digestible macromolecules, that form polymeric chain, suffer enzymatic scission. This is followed by metabolism of scission parts, leading to progressive enzymatic degradation of macromolecules from chain ends. Instead, macromolecular oxidative cleavage occurs, inducing fragments metabolism. Anyway, chain fragments become small enough to be converted by microorganisms [13,20]. Enzymes are catalytic proteins that decrease activation energy of molecules favoring chemical reactions. Those proteins have large diversity and marked specificity, but are easily denatured by heating, radiation, surfactants, among others [31]. In Fig. 19 general mechanism of biodegradation of polymeric materials is presented.

According to Liu et al. [18], hydrolytic degradation of PCL and PLLA has been studied extensively. PLLA artifacts degradation is faster in the inner part than in the surface due to autocatalytic effect of carboxyl end groups. In the case of PCL, hydrolytic degradation is very low because of hydrophobicity and crystallinity. Authors reported that, in presence of proteinase K, PLLA degraded preferably at L-lactil units. Furthermore, enzymatic degradation occurred preferably on amorphous region of semi-crystalline PLLA polymers [11,18,19].

According to Lenglet et al. [19], hydrolytic degradation is a mass phenomenon and polyesters degradation with high size is auto catalyzed by carboxyl end groups initially present, or generated by ester bond cleavage. The three most important discoveries about polyester degradation performed in the last decade were about faster degradation in the inner portion of the sample and that degradation induces morphology and composition alteration. On the other hand, enzymes are macromolecules and cannot penetrate in a solid material. Then,
enzymatic degradation occurs in two steps: adhesion of enzyme on the surface of sample followed by scission of polymeric chain catalyzed by enzyme that generally results in small alterations of properties of polymeric matrix. According those authors, highly crystalline PCL can be fully degraded in a couple of days in presence of Pseudomonas lipase, while hydrolytic degradation can take several years in 37°C (average temperature of human body). Kulkarni et al. [32] have cited that Pseudomonas cepacia lipase accelerates significantly PCL degradation. Interface activation of enzymes lipase type results mainly in conformational alteration of enzymes. Reaching substrate surface, they expose their active site and provide hydrophobic surface to the interaction with substrate molecular chains. The authors cited that several publications deal with the fundamentals of the theory of hydrolytic degradation and erosion of solid polymers. The basic modes, the surface erosion and the bulk degradation, depend on the relation between the rate of water/enzyme diffusion into the polymer, the rate of chain cleavage by water ions/enzymes, and the rate of transportation of scission products out of the solid. The rate of water diffusion into a polymer solid is strongly influenced by a number of structural parameters, its porosity, the crystallinity, the surface roughness, the hydrophobicity and the size of the sample. Most authors treat the enzymatic degradation of polymer solids exclusively as surface process. For hydrophilic enzymes it is usually considered to be difficult to penetrate into a hydrophobic polymer.

Loo et al. [11] cited that the rate of hydrolytic degradation for biopolymers like PGLA and PLLA is controlled by altering their physical properties; such as their molecular weights, degree of crystallinity and glass transition temperature ($T_g$). As mentioned previously, radiation has been known to alter the physical properties of polymers through main-chain scission and cross-linking. Semi-crystalline polymers, such as PLLA, are nonhomogeneous with a two-phase system consisting of amorphous and crystalline regions. During irradiation, energy is deposited uniformly and radicals are formed throughout the polymer in both the amorphous and crystalline regions. However, crystalline regions consist of chains that were more oriented and closely packed compared to the more open amorphous regions. As a result, oxygen, stabilizers and specific active radical species are excluded from the crystalline phase,

Figure 19. General mechanism of biodegradation of polymeric materials [13].
and the irradiation chemical reaction paths in the amorphous and crystalline phases will therefore be different. According to Loo et al. [11], due to the close packing of the crystalline structure, the poor diffusion of oxygen into the crystalline region limits the formation of peroxyl free radicals and thus, the extent of chain scission. The “cage effect” also encourages the recombination of free radicals in the crystalline region. These factors play an important role in reducing the extent of e-beam degradation in PLLA.

5. Conclusion

Results of degradability test, enzymatic and in simulated compost soil, indicate that studied materials suffered accentuated degradation in enzymes presence and are not affected by negatively by radiation processing. Even though coconut fibers addition had slightly reduced degradation process, composites keep degrading through time. Artifacts produced utilizing the studied materials can be processed by ionizing radiation up to 100 kGy radiation doses without detriment of their biodegradability.

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References

[1] Tsuji, H, & Ikada, Y. Blends of aliphatic polyesters. I. Physical properties and morphologies of solution-cast blends from poly (DL-lactide) and poly(ε-caprolactone). Journal of Applied Polymer Science (1996). , 60(1), 2367-2375.

[2] Kammer, H. W, & Kummerlowe, C. (1994). Poly (ε-caprolactone) Comprising Blends-Phase Behavior and Thermal Properties, in Finlayson, K. (ed.) Advances in Polymer Blends and Alloys Technology, Technomicv, USA, 5, , 132-160.

[3] Dell’Erba RGroeninckx G., Maglio G., Malinconico M., Migliozi A. Imiscible polymer blends of semicrystalline biocompatible components: thermal properties and phase morphology analysis of PLLA/PCL blends. Polymer (2001 4). , 2001(42), 1-7831.

[4] Yoshii, F, Darvis, D, Mitomo, H, & Makuuchi, K. Crosslinking of poly (ε-caprolactone) by radiation technique and its biodegradability. Radiation Physics and Chemistry (2000 5). , 2000(57), 1-417.

[5] Zhang, J, Duan, Y, Sato, H, Tsuji, H, Noda, I, Yan, S, & Ozaki, Y. Crystal modifications and thermal behavior of poly (L-lactic acid) revealed by infrared spectroscopy. Macromolecules (2005 3). , 2005(38), 1-8012.

[6] Mochizuki, M, & Hirami, M. Structural effects on the biodegradation of aliphatic polyesters. Polymers for Advanced Technology (1997 8). , 1997(8), 1-203.

[7] Michler, G. H. ed) ((2008). Electron Microscopy of Polymers, Springer-Verlag.

[8] Sawyer, L. C, Grubb, D. T, & Meyers, G. F. eds) ((2008). Polymer Microscopy 3rd ed, Springer.

[9] Azevedo, H. S, & Reis, R. L. (2005). Understanding the enzymatic degradation of biodegradable polymers and strategies to control their degradation rate. In: Reis RL, Román JS (eds). Biodegradable Systems in Tissue Engineering and Regenerative Medicine. CRC, Boca Raton, , 177-197.

[10] Chmielewski, A. G. New Trends in radiation processing of polymers, In: International Nuclear Atlantic Conference; Encontro Nacional de Aplicações Nucleares, 7th, aug. sept. 2, 2005, Santos, SP. Anais... São Paulo: ABEN, (2005). , 28.

[11] Loo, J. S. C, Ooi, C. P, & Boey, F. Y. C. Degradation of poly(lactide-co-glycolide) (PLGA) and poly(l-lactide) (PLLA) by electron beam radiation. Biomaterials (2005). , 2005(26), 1-1359.

[12] Kantoglu, Ö, & Güven, O. Radiation induced crystallinity damage in poly(L-lactic acid), Nuclear Instruments and Methods in Physical Research B (2002 1). , 2002(19), 1-259.
[13] Müller, R. J. ((2005). Biodegradability of Polymers: Regulations and Methods for Testing in: STEINBÜCHEL, A. (ed.), Biopolymers- General Aspects and Special Applications, Wiley-VCH Verlag GmbH & Co. KgA, n. 19, , 10, 365-374.

[14] Kuo, S-W. Hydrogen-bonding in polymer blends. Journal of Polymer Research (2008 1). , 2008(15), 1-459.

[15] Tsuji, H, & Ishizaka, T. Blends of aliphatic polyesters, VI. Lipase-catalyzed hydrolysis and visualized phase structure of biodegradable blends from poly(e-caprolactone) and poly(L-lactide). International Journal of Biological Macromolecules (2001 2). , 2001(29), 1-83.

[16] Kikkawa, Y, Suzuki, T, Tsuge, T, Kanesato, M, Doi, Y, & Abe, H. Phase structure and enzymatic degradation of poly(L-lactide)/atactic poly(3-hydroxybutyrate) blends: an atomic force microscopy study. Biomacromolecules (2006). , 2006(7), 1-1921.

[17] Nishino, T, & Hirao, K. Kotera M. X-ray diffraction studies on stress transfer of kenaf reinforced poly(L-lactic acid) composite. Composites: Part A (2006). , 2006(37), 1-2269.

[18] Liu, L, Li, S, Garreau, H, & Vert, M. Selective Enzymatic Degradations of Poly(L-lactide) and Poly(ε-caprolactone) Blend Films. Biomacromolecules (2000). , 2000(1), 1-350.

[19] Lenglet, S, Li, S, & Vert, M. Lipase-catalysed degradation of copolymers prepared from e-caprolactone and DL-lactide. Polymer Degradation and Stability (2009 9). , 2009(94), 1-688.

[20] Kolybaba, M, Tabil, L. G, Panigrahi, S, Crerar, W. J, Powell, T, & Wang, B. (2003). Biodegradable polymers: past, present and future. 2003 CSAE/ASAE Annual Interceccional Meeting Sponsered by the Red Rive Section of ASAE. Fargo, North Dakota, USA, October , 3-4.

[21] Calado, V, Barreto, D. W, & Almeida, D. J.R.M. The effect of a chemical treatment on the structure and morphology of coir fibers. Journal of Materials Science Letters (2000). , 2000(19), 1-2151.

[22] Almeida, D, Calado, A. L. F. S, & Barreto, V. D.W. Acetilação da fibra de bucha (Luf-fa cylindrica) Polímeros: Ciência e Tecnologia (2005 1). , 2005(15), 1-59.

[23] Spinks, J. W. T, & Woods, R. J. An Introduction to Radiation Chemistry. 3rd ed. USA: John Wiley and Sons; (1990).

[24] Calil, M. R, Gaboardi, F, Bardi, M. A. G, Rezende, M. L, & Rosa, D. S. Enzymatic degradation of poly(ε-caprolactone) and cellulose acetate blends by lipase and α-amilase. Polymer Testing (2007 2). , 2007(26), 1-257.
[25] Sivalingam, G, Vijayalakshmi, S. P, & Madras, G. Enzymatic and thermal degradation of poly(e-caprolactone), poly(D,L-lactide, and their blends. Industrial & Engineering Chemistry Research (2004 4). , 2004(43), 1-7702.

[26] Cottam, E, Hukins, D. W. L, Lee, K, Hewitt, C, & Jenkins, M. J. Effect of sterilization by gamma irradiation on the ability of polycaprolactone (PCL) to act as a scaffold material. Medical Engineering & Physics (2009 3). , 2009(31), 1-221.

[27] Maharana, T, Mohanty, B, & Negi, Y. S. Melt-solid polycondensation of lactic acid and its biodegradability. Progress in Polymer Science (2009 3). , 2009(34), 1-99.

[28] Salazar, V. L. P, & Leão, A. L. Biodegradação das fibras de coco e de sisal aplicadas na indústria automotiva. Revista Energia na Agricultura (2006). , 2006(21), 2-99.

[29] Alauzet, N, Roussos, S, Garreau, H, & Vert, M. Microflora dynamics in earthworms casts in an artificial soil (biosynthesol) containing lactic acid oligomers Brazilian archives of biology and technology (2001 4). , 2001(44), 2-113.

[30] Lotto, N. T, Calil, M. R, Guedes, C. G. F, & Rosa, D. S. The effect of temperature on the biodegradation test. Materials Science and Engineering C (2004 2). , 2004(24), 1-659.

[31] Lucas, N, Bienaime, C, Belloy, C, Queneudec, M, Silvestre, F, & Nava-saucedo, J. E. Polymer biodegradation: mechanisms and estimation techniques. Chemosphere (2008 7). , 2008(73), 1-429.

[32] Kulkarni, A, Reiche, J, Hartmann, J, Kratz, K, & Lendlein, A. Selective enzymatic degradation of poly(e-caprolactone) containing multiblock copolymers. European Journal of pharmaceuticals and biopharmaceutics (2008 6). , 2008(68), 1-46.
