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# Ionizing Radiation Effect on Morphology of PLLA: PCL Blends and on Their Composite with Coconut Fiber

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## 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( $\epsilon$ -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 (Tsuji & Ikada, 1996; Kammer & Kummerlowe, 1994; Dell’Erba et al., 2001; Yoshii et al., 2000; Zhang et al., 2005). The controlled degradation of polymers is sometimes desired for biomedical applications and environmental purposes (Michler, 2008).

PLLA is a poly( $\alpha$ -hydroxy acid) and PCL is a poly( $\omega$ -hydroxy acid) (Tsuji & Ikada, 1996). PLLA is a hard, transparent and crystalline polymer (Mochizuki & Hirami, 1997). 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 (Kammer & Kummerlowe, 1994). 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. Ionizing radiation exposure induces to crosslinking or scission of polymer main chain (Broz et al., 2003), besides other chemical alterations. Nature of those alterations is affected by chemical structure of polymer, and also by gaseous compounds present, as oxygen. Irradiation in the presence of air or oxygen leads to oxidized products formation that normally are undesirable, being less thermally stable and decreasing crosslinking degree by reaction of polymeric radicals (Charlesby et al., 1991).

The market for biodegradable polymers had shown strong growth from 2001 up to 2005. A number of major plant expansions for commercial scale production had been planned. The major classes of biopolymers, polylactic acid and aliphatic-aromatic co-polyesters has been used in a wide variety of niche applications, particularly for manufacture of rigid and flexible packaging, bags and sacks and foodservice products. In 2005, starch-based materials were the largest class of biodegradable polymer and polylactic acid (PLA) was the second

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largest material class followed by synthetic aliphatic-aromatic co-polyesters. Product development and improvement has a crucial role to play in the further development of the biodegradable polymers market. Biodegradable polymers can be found in a wide range of end use markets. Continued progress in terms of product development and cost reduction will be required before they can effectively compete with conventional plastics for mainstream applications. The main markets for PLA are thermoformed trays and containers for food packaging and food service applications. In 2005, packaging was the largest sector with 39% of total biodegradable polymer market volumes. Loose-fill packaging was the second largest sector, followed by bags and sacks. Fibers or textiles is an important sector for PLA, and accounted for 9% of total market volumes. Others include a wide range of very small application areas, the most important of which are agriculture and fishing, medical devices, consumer products and hygiene products. While the cost of some biodegradable plastics is high compared to conventional polymers, from a marketing perspective, it is important not only to consider the material cost, but also all associated costs, including the costs of handling and disposal, which are of course lower for biodegradable plastics. Users of biodegradable plastics can differentiate themselves from the competition by demonstrating how innovative and proactive they are for the benefit of the environment (Platt, 2006).

Poly(lactic acid) is a biodegradable polymer derived from lactic acid. It is a highly versatile material and is made from 100% renewable resources like corn, sugar beet, wheat and other starch rich products. The homopolymer of L-lactide is a semicrystalline polymer. Due to high costs, the focus was initially on the manufacture of medical grade sutures, implants and controlled drug release applications. PLA has many potential uses, including many applications in the textile and medical industries as well the packaging industry.

From a commercial point of view the most important synthetic biodegradable aliphatic polyester was traditionally polycaprolactone (PCL). The ring opening polymerization of  $\epsilon$ -caprolactone yields a semicrystalline polymer, which is regarded as tissue compatible and was originally used in the medical field as a biodegradable suture in Europe. Polycaprolactone aliphatic polyesters have long been available commercially for use as adhesives, compatibilizers, modifiers and films, as well as medical applications. Caprolactone limits moisture sensitivity, boosts melt strength, and helps to plasticize the starch (Platt, 2006).

In order to improve some desirable properties two or more polymers can be mixed to form polymeric blends (Utracki, 1989). 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 (Michler, 2008). However, according to Michler (2008), usually different polymers are incompatible. Improved properties can be only realized if the blend exhibits optimum morphology. According to Sawyer (2008), 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.

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 (Dell'Erba et al., 2001; Michler, 2008; Nakayama & Tanaka, 1997) and are very important to define the characteristics of the obtained material. One common feature of semicrystalline polymers is a hierarchical morphology. The scales of structural details within them range from nanometers to millimeters. Under certain conditions, macromolecules are able to form periodic structures that involve adjacent chains or chain segments. By repeated folding of a flexible polymer chain results in densely packed and highly ordered domains. Polymers normally are partially crystalline, highly ordered domains will coexist with regions of an amorphous phase and a crystalline fraction with identical chemical compositions but divergent physical properties (Michler, 2008). Moreover, the structural modifications induced by ionizing radiation may alter the morphology of the samples.

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 (Dell'Erba et al., 2001). Chemical structure influences the biodegradation of solid polymers. Enzymatic and non enzymatic degradations occur easier in the amorphous region (Mochizuki & Hirami, 1997; Tsuji & Ishizaka, 2001). The crystallinity and the resulting morphology are usually controlled by using either different proportions of stereoisomers (enantiomers, e.g. L-lactide and D-lactide) of the same monomer or a defined ratio of comonomers of related polyesters (Michler, 2008).

The morphology of the blends affects also the biodegradation of the polymers. 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 (Dell'Erba et al., 2001; Michler, 2008). Kikkawa et al. (2006) 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. In particular, surface structure and morphology of biodegradable polymer blends have a great impact on the enzymatic degradation behavior by enzymes. According to Michler (2008), a high degree of crystallinity yields low degradation rates since it has been shown that hydrolytic degradation (cleavage of ester bonds) preferentially occurs in the amorphous regions.

Plastic solid waste has become a serious problem recently concerning environmental impact. In this scenario, preparation of polymers and composites based on coconut husk fiber would lead to a reduction on the cost of the final product. Additionally, it will reduce the amount of agribusiness waste disposal in the environment. In Brazil, coconut production is around 1.5 billion fruits by year in a cultivated area of 2.7 million hectares, but the coconut husk fiber has not been used much for industrial applications. According to Sawyer (2008), composites can contain short or continuous fibers, inorganic or organic. Even though according to Michler (2008), the word "composite" should only be applied to polymers with inorganic components, in this chapter it will be applied to the mixture of polymeric blend and natural coconut fiber.

It is worthy of note that the use of natural fibers as reinforcement in polymeric composites is an important research field that has been growing in the last decades, (Kapulskis et al, 2006;

Martins et al., 2006; Tomczak et al., 2007). Thus, by 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 (Chmielewski, 2005).

The structures and morphologies of polymers have been under investigation for more than 60 years. Scanning electron microscopy (SEM) was introduced in the 1960's, and has been used to investigate fracture of surfaces, phase separation in polymer blends and crystallization of spherulites. Several improvements have been made in electron generation and electron optics that have enhanced the resolution power. Also, computerized SEM led to the introduction of the digital scanning generator for digital image recording and processing. Consequently, SEM is at present the most popular of the microscopic techniques. This is because of the user-friendliness of the apparatus, the ease specimen preparation, and the general simplicity of image interpretation. The limitation is that only surface features are easily accessible. Furthermore, chemical analysis of different elements is usually possible with SEM (energy dispersive or wavelength dispersive analysis of X-rays, EDXA, WDXA) (Michler, 2008). According to Sawyer (2008), SEM is used to evaluate features as the size, distribution, and adhesion of the fibers or particles, their adhesion to the matrix play a major role in revealing the strength and toughness enhancement. Regarding to the studied material, coarse structures such as larger particles in a matrix can easily be studied at low temperature (brittle) fracture surfaces in the SEM, since the fracture path follows the shape of the particle (Michler, 2008) considering that from a practical point of view, a good indicator of the degree of compatibility is the heterogeneity of the polymer system (e.g how the sizes of the dispersed domains depend on the processing conditions).

The objective of this chapter is to present the effect of ionizing radiation on the morphology of PLLA:PCL blend and composites containing coconut fiber. SEM and field emission (FE) SEM micrographs were taken of non irradiated and irradiated samples with gamma rays and electron beam.

## 2. Experimental

### *Coconut fiber*

Coconut fibers were from three different origins: Embrapa- Empresa Brasileira de Pesquisa Agropecuária, Paraipaba region, Ceará; Projeto Coco Verde - Quissamã, Rio de Janeiro; Poematec - Ananindeua, Pará.

Size reduction of the coconut fibers was carried out using helix mill Marconi - model MA 680, from Laboratório de Matéria-prima Particulados e Sólidos Não Metálicos - LMPSol, Departamento de Engenharia de Materiais of 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 0.417mm fiber 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  $\text{Na}_2\text{SO}_3$  2% aqueous solution for 2h using ultrasound. Fibers from Embrapa were washed several times with tap water and finally, three times with deionized water, as described by Calado et al. (2000).

Fiber acetylation was performed as described by d'Almeida et al. (2005). 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. Set 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.

Fiber residue of non irradiated and irradiated samples were obtained using a furnace at  $600^\circ\text{C}$ , air atmosphere, by 2 hours. Residues were analyzed in a Scanning Electron Microscope, SEM, Jeol, JXA-6400, at Centro Tecnológico da Marinha em São Paulo (CTMSP). It was used Energy Dispersion Spectroscopy, EDS, to analyze chemical elements present in the residues.

#### *Preparation of blend sheets*

PLLA pellets were dried in a vacuum oven at  $90^\circ\text{C}$  and PCL pellets were dried at  $40^\circ\text{C}$  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 (60mm width and 1.05mm thickness). T-die temperature was set at  $205^\circ\text{C}$  for PLLA homo-polymer and its blends, and at  $90^\circ\text{C}$  for PCL. Extruded sheets were quenched using a water bath set at room temperature. The take up speed was selected at  $0.35 \text{ m min}^{-1}$ . 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.

#### *Preparation of composite pellets and sheets*

PCL (pellets,  $\bar{M}_w=2.14 \cdot 10^5 \text{ g mol}^{-1}$ ;  $\bar{M}_w/\bar{M}_n=1.423$ ), PLLA (pellets,  $\bar{M}_w=2.64 \cdot 10^5 \text{ g mol}^{-1}$   $\bar{M}_w/\bar{M}_n=1.518$  – Gel Permeation Chromatographic values) and dry coconut fiber (from Embrapa, 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 PLLA:PCL 80:20 (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, PLLA:PCL 80:20 (w:w) blend and composites containing 5 and 10% untreated and chemically treated coconut fiber were prepared using Ikeda hot press equipment of JAEA– Japan Atomic Energy Agency. Mixed pellets of samples were preheated at  $195^\circ\text{C}$  for 3 min and then pressed by under heating at the same temperature for another 3 min under pressure of  $150 \text{ kgf cm}^{-2}$ . The sample was then cooled in the cold press using water as a coolant for 3 min.

#### *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<sup>-1</sup>. Samples were cut 10 × 100 cm<sup>2</sup>, and irradiated at room temperature in air.

#### *Electron beam irradiation*

Hot pressed sheets were irradiated using a electron beam accelerator (E=2 MeV, 2 mA) applying radiation doses from 10 kGy to 500 kGy with a dose rate of 0.6 kGy s<sup>-1</sup>, at JAEA, Takasaki, Japan.

#### *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 cryogenic fractured surface of the blends sheet were taken after 4-5 min gold coating.

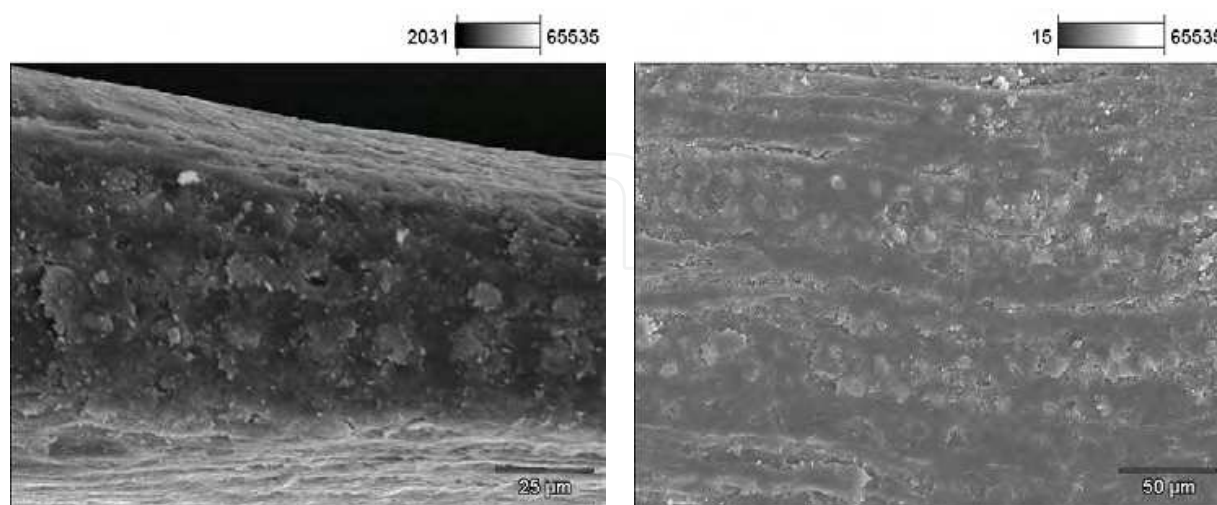
SEM micrographs of the irradiated homopolymers and blends sheets; and coconut fibers surfaces from cryogenic fractured samples were obtained using a scanning electron microscope model JXA-6400 (JEOL) at Centro Tecnológico da Marinha em São Paulo.

#### *Field Emission Scanning Electron Microscopy (FE-SEM)*

Photomicrographs of the, cryogenic fractured, non-irradiated and irradiated samples were taken using a field emission scanning electron microscope, JEOL, JSM - 7401F, acceleration voltage 1.0 kV at Central Analítica IQ-USP.

### **3. Results and discussion**

Figure 1 shows scanning electron micrographs of coconut fiber surface, as received samples from Embrapa.

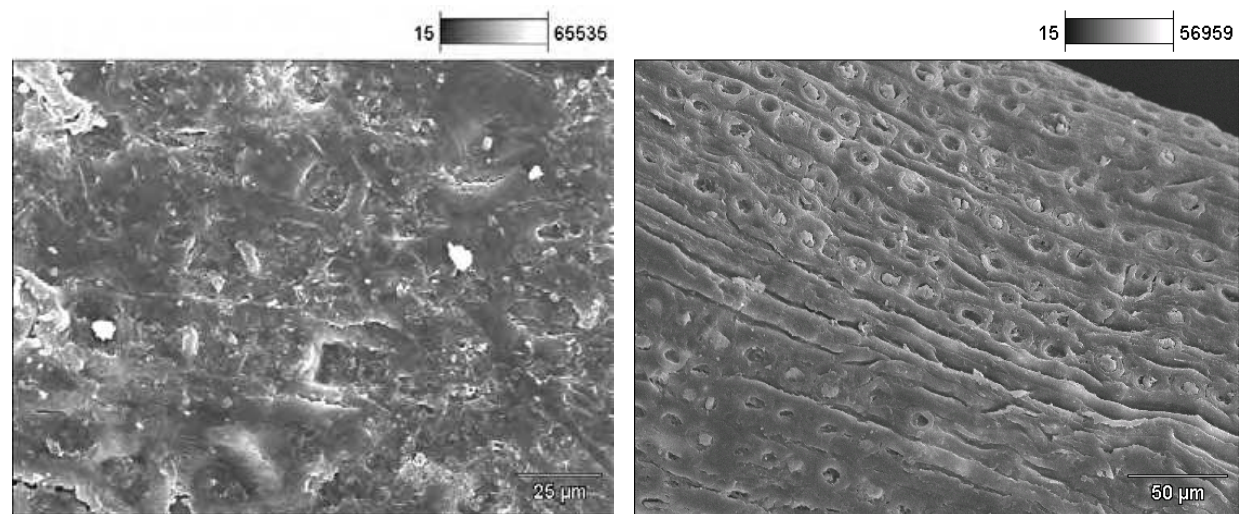


Acceleration voltage: 20.0 kV Magnification: 700×      Acceleration voltage: 20.0 kV Magnification: 350×

Fig. 1. Scanning electron micrographs of coconut fiber surface, as received from Embrapa.

There are some studies involving chemical treatment of vegetal fibers to improve its compatibility to polymers (Kapulskis et al, 2006; Abdul-Khalil & Rozman, 2000; Lee et al., 2004). Cell wall of a plant in the dry state consist mainly of carbohydrates combined to lignin, and few quantities of protein, starch and inorganic compounds, chemical composition varies from plant to plant and through different parts of the same plant (Rowell et al., 2000). The lignocellulosic fibers characteristics vary considerably with the place where they are produced, and possess different chemical compositions that affect their physical and chemical properties (Tomczak et al., 2007).

According to Calado et al. (2000), coconut coir fiber treated with  $\text{Na}_2\text{SO}_3$  suffers lignin removal from surface and its roughness increases. This increase of surface roughness improves their adhesion due to promotion of mechanical interaction between fibers and polymeric matrix. In this sense, scanning electron micrographs of coconut fibers surface, chemically treated with  $\text{Na}_2\text{SO}_3$  are shown in Figure 2.



Acceleration voltage: 20.0 kV Magnification 600× Acceleration voltage: 20.0 kV Magnification: 350×

Fig. 2. Scanning electron micrographs of coconut fibers surface from Embrapa , chemically treated with  $\text{Na}_2\text{SO}_3$ .

Chemical treatment with anhydride acetic reduces the number of hydroxyl radicals, as shown in Figure 3. This treatment would reduce cellulose molecules polarity and then would improve the compatibility with thermo rigid matrix used in composites.

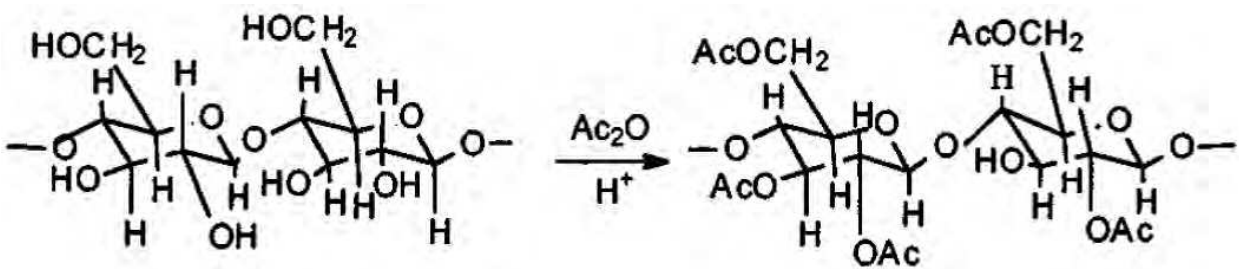
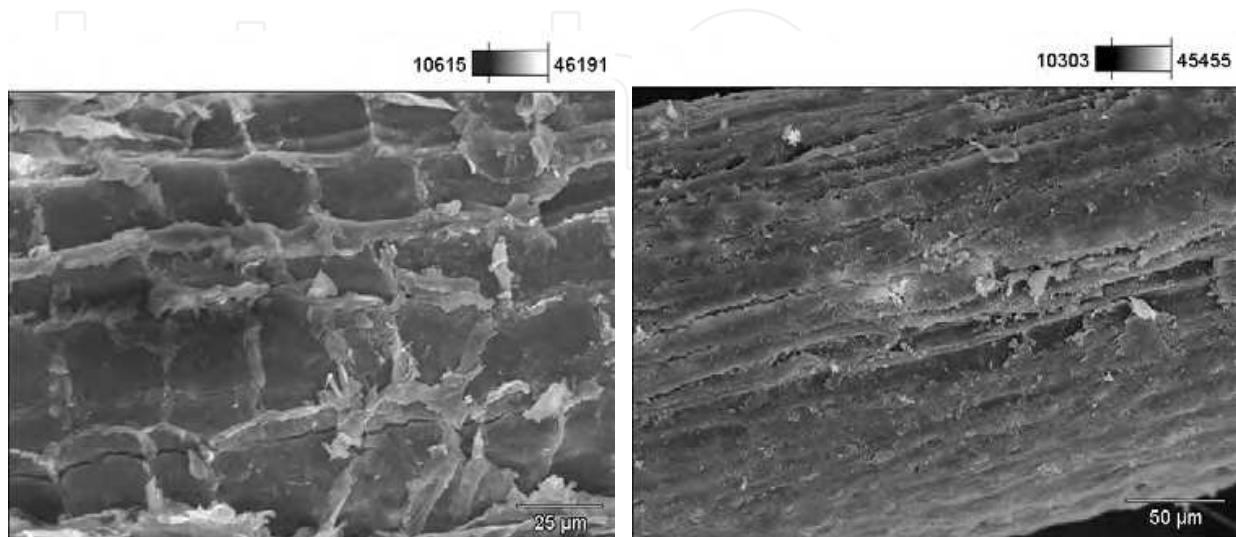


Fig. 3. Cellulose acetylation reaction (Calado et al., 2000).



Calado et al. (2000) observed clear difference on the morphologies of non treated and chemical treated surfaces of coir fibers. Same behavior was observed on the fibers studied in this chapter.

It was possible to observe roughness increase on the surface treated with  $\text{Na}_2\text{SO}_3$  and anhydride acetic, as shown in Figure 4.



Acceleration voltage: 20.0 kV Magnification: 600× Acceleration voltage: 20.0 kV Magnification: 350×

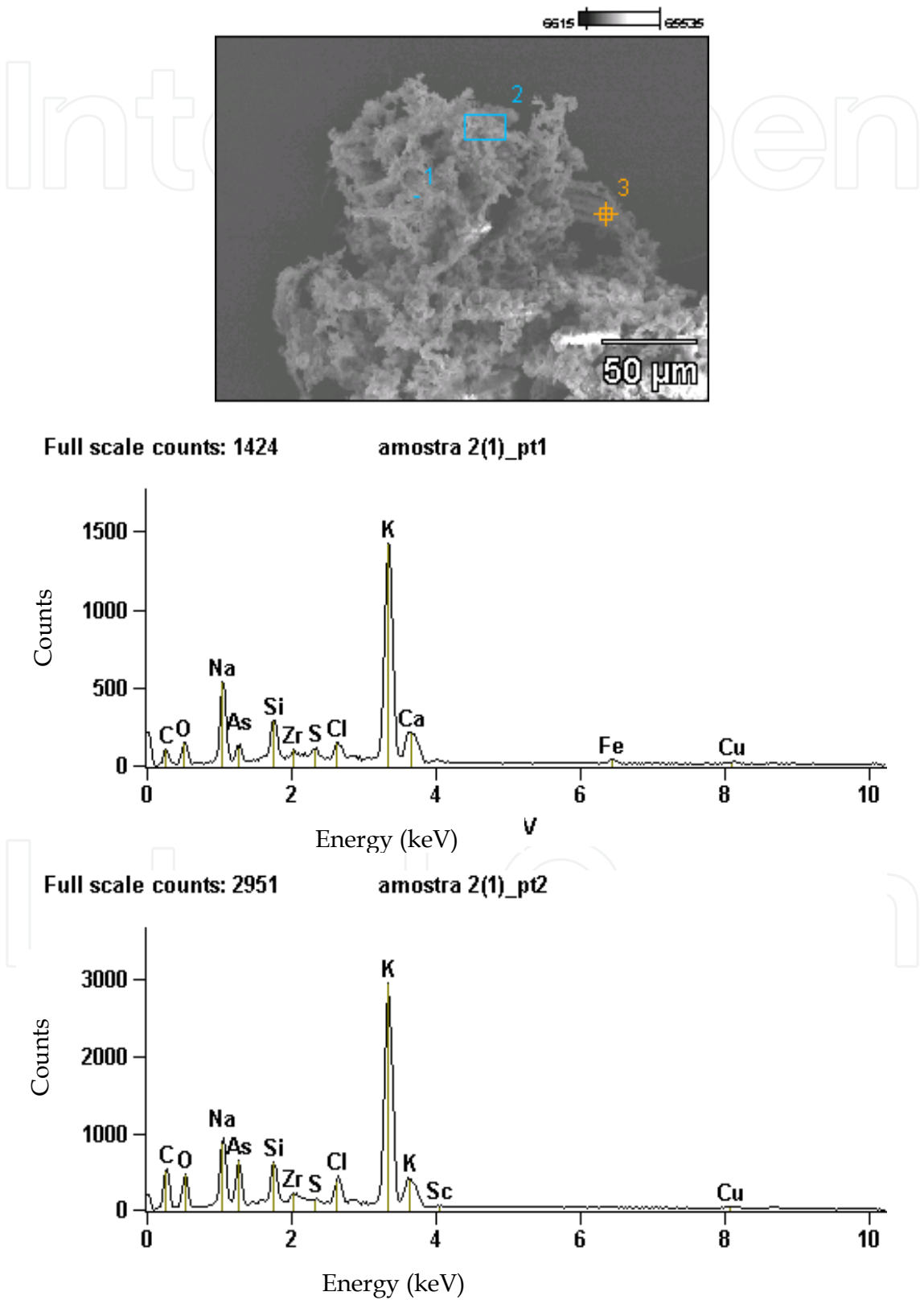
Fig. 4. Scanning electron micrographs of coconut fibers surface from Embrapa, chemically treated with  $\text{Na}_2\text{SO}_3$  and anhydride acetic, respectively.

X rays spectra by EDS of Embrapa coconut fiber, non irradiated with 0.297 mm up to 0.417 mm size, are shown in Figure 5. It was possible to identify that chemical composition of the residue varied for the same fiber. It can be explained by the fact that chemical composition varies from plant to plant and also through different parts of the same plant (Rowell et al., 2000; Severiano et al., 2010).

In the residue of thermal decomposition in air of fibers from three different origins, most common elements found were K, Na, Si, Ca and, in some cases, Fe. In the literature, they found P, Mg and , in small concentrations, Cu, Zn, Mn (Rosa et al., 2001), in addition to Cl, S, Br e Rb (Mothé & Miranda, 2009) that were not observed in samples in this study. This variation can be attributed to soil where coconut tree was grown. Peak that had attributed to Zr, in fact is due to P, as they appear at the same channel of energy and, it is more probable to find P in higher quantity in soil than Zr. Peak that was attributed to As observed in some spectra was due to coating process used to allow image formation.

Scanning electron micrographs of surfaces of cryogenic fractured non irradiated as extruded blend samples were taken. As extruded PCL micrograph shows a homogeneous morphology, as shown in Figure 6. The as extruded PCL:PLLA 50:50 micrograph shows spheres with different sizes and shapes, as shown in Figure 7. According to Michler (2008), when a polymer is cooled down from the melt, the (primary) crystallization starts from initial points that are randomly distributed in the volume. Such starting points are either homogeneous or heterogeneous nuclei (i.e. nucleating agents, impurities, or filler particles). This radial growth results in a characteristic arrangement of lamellae. The superstructures

(spherulites and sheaf-like boundless of lamellae) come in a variety of forms depending on the polymer and its crystalline structure. These superstructures generally form a texture consisting of one or more spherulite types with a characteristic spherulite size distribution.



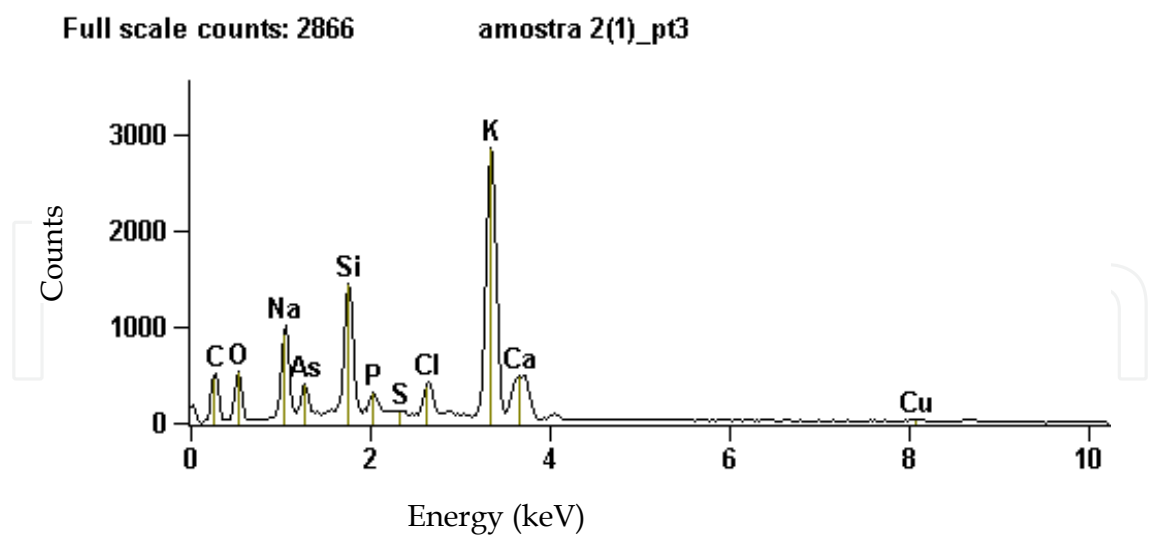


Fig. 5. Scanning electron micrograph of non irradiated Embrapa coconut fiber (0.297 and 0.417 mm) residue and X ray spectra by EDS (points 1, 2 and 3).

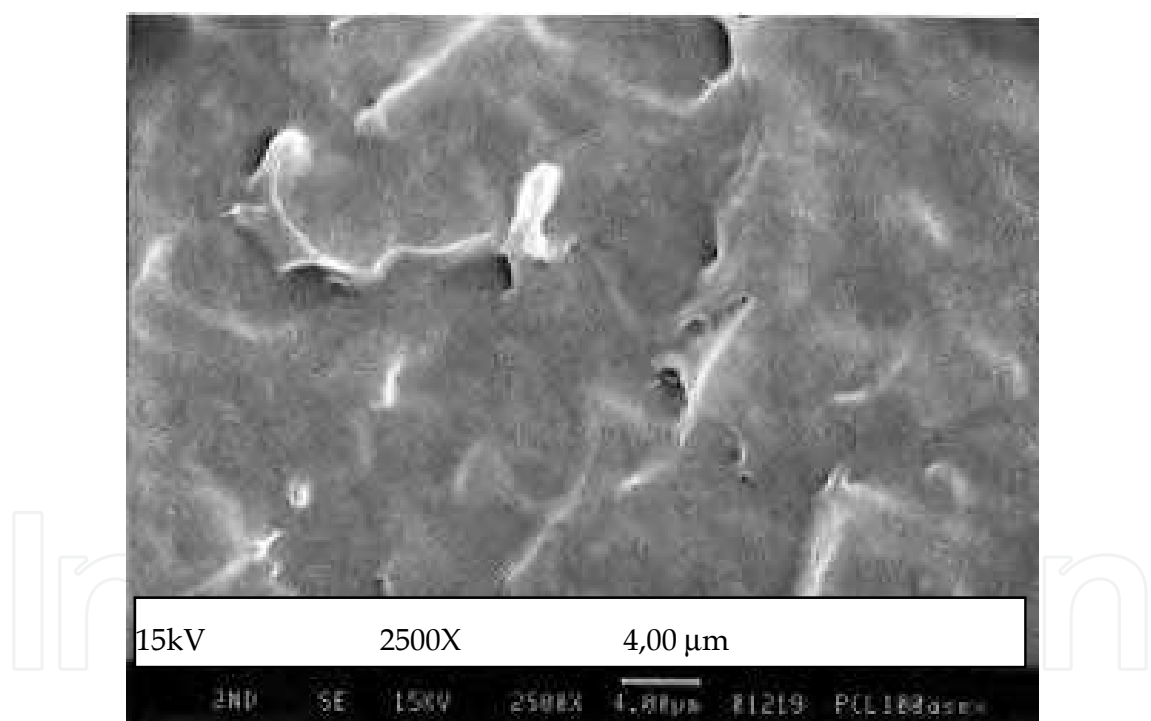


Fig. 6. Scanning electron micrograph of as extruded PCL, cryogenic fractured sample.

It is possible to observe the continuous PLLA-rich phase and the PCL-rich dispersed phase with a maximum domain size of 1.5  $\mu\text{m}$ , as visualized before by Tsuji et al. (2001) in PCL:PLLA solution-cast blends. The PCL-rich phase is homogeneously dispersed in the PLLA matrix. One can observe some cracks or voids in the PLLA film probably caused by the temperature of processing, as shown in Figure 8. It has mentioned before that the degradation of aliphatic polyesters can occur because of melting at high temperatures (Yoshii et al., 2000; Kodama et al., 1997).

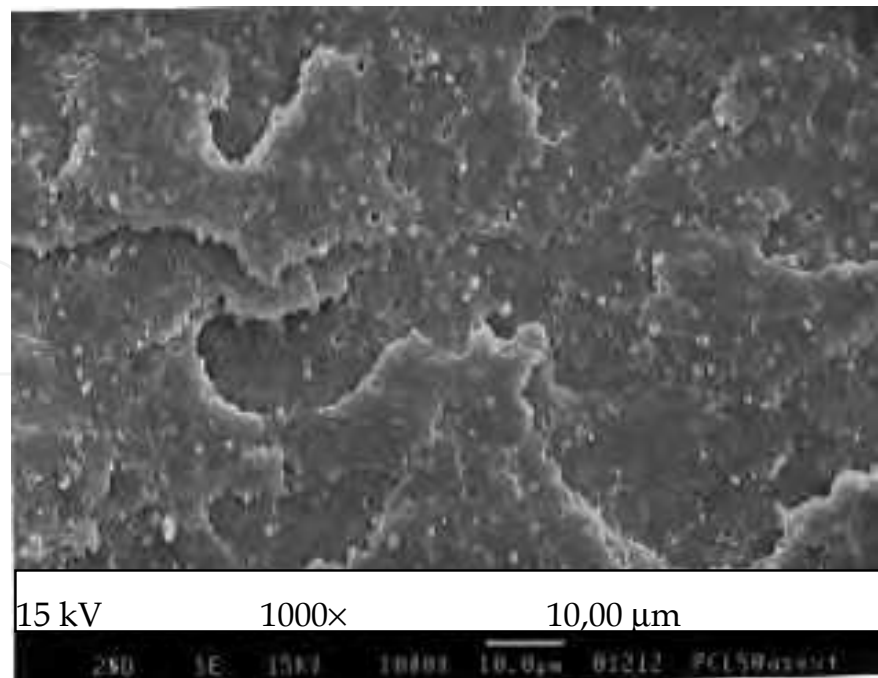


Fig. 7. Scanning electron micrograph of as extruded PCL:PLLA 50:50 (w:w), cryogenic fractured sample.

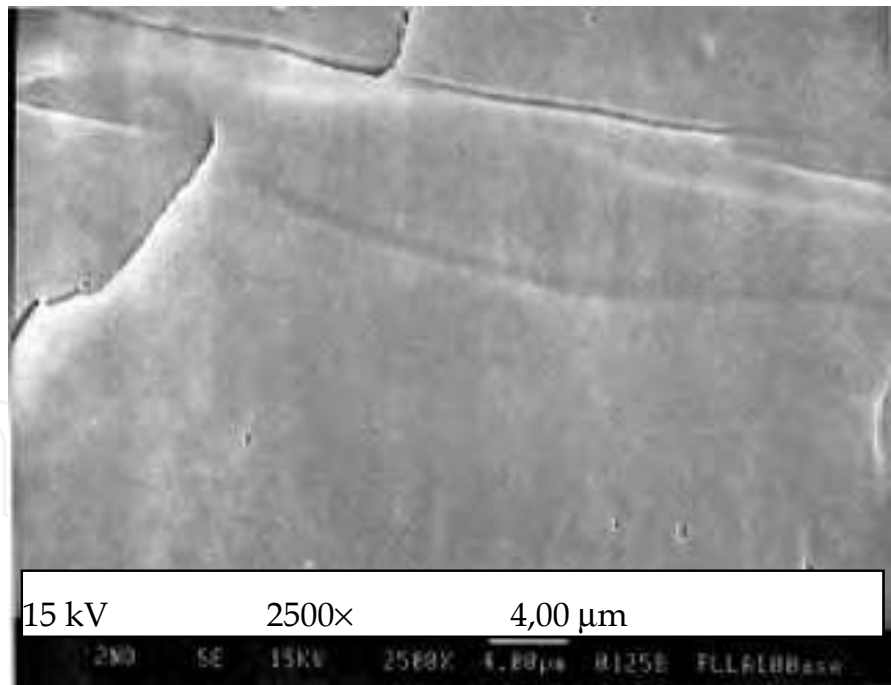


Fig. 8. Scanning electron micrograph of as extruded PLLA, cryogenic fractured sample.

Micrographs of annealed PLLA (Figure 9) and PCL:PLLA 50:50 (w:w) (Figure 10) shows changes in the morphology due to the crystallization of PLLA. Utracki (1989) explained that depending on the crystallization conditions various types of morphology can be obtained, which proceeds through melt, nucleation, lamellar growth and, spherulitic growth.



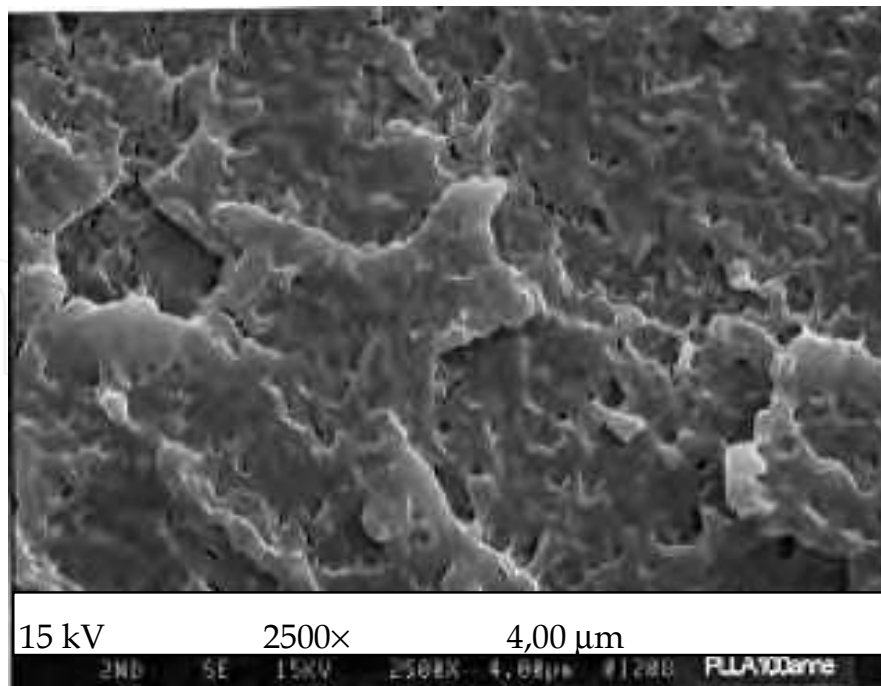


Fig. 9. Scanning electron micrograph of *annealed* PLLA, cryogenic fractured sample.

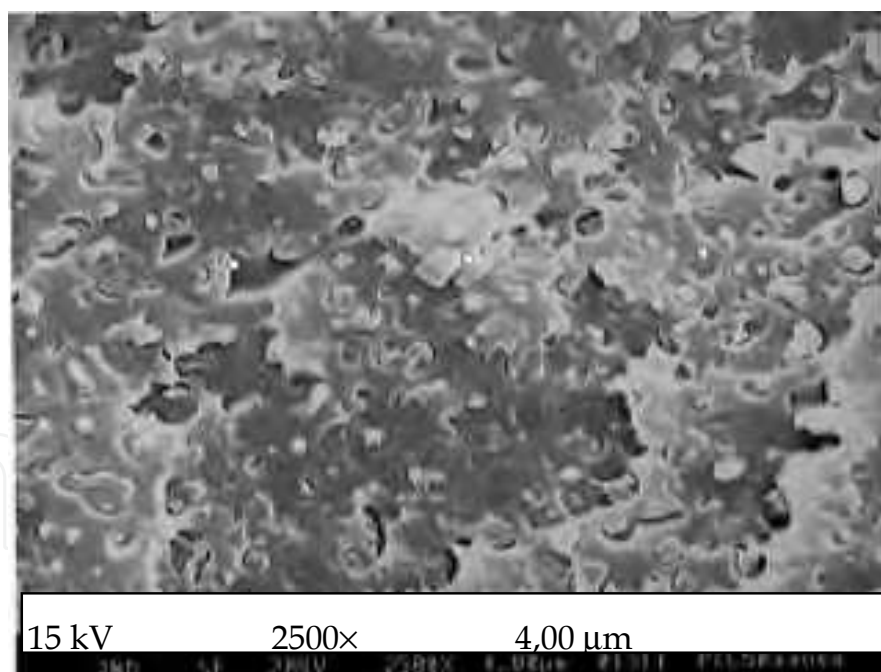


Fig. 10. Scanning electron micrograph of *annealed* PCL:PLLA 50:50 (w:w), cryogenic fractured sample.

Although the temperature of annealing was lower than the PLLA melting temperature ( $T_m$ ), the thermal treatment allowed the crystallization of PLLA. 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 verify some

morphological changes. The spheres are apart from the matrix, and in addition the matrix was changed due to the crystallization of PLLA. The blends are not miscible and the after extrusion 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.

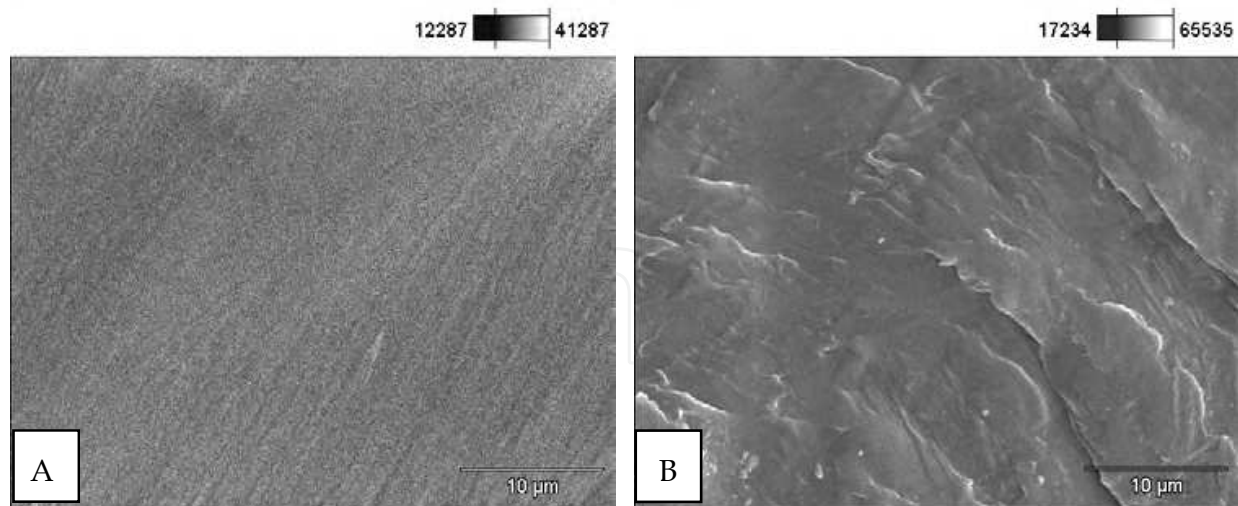
In preliminary studies by differential scanning calorimetry (DSC) no change in the PLLA melting temperature was observed by increasing the PCL content in the blends. It was observed that, as PCL amount increased, PCL  $T_m$  peak increased in the region of the glass transition temperature of PLLA (Kodama et al., 1997). Although the immiscibility occurs, 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.

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. (2001) 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 favoring 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 (Broz et al., 2003). Also the orientation of crystallites in the blends was observed by x-ray diffraction, PLLA crystallizes in the  $\alpha$  form with  $10_3$  helical conformation (Zhang et al., 2005). The thermal treatment increases the quantity of spheres, it was possible to notice some ellipsoids. This suggests that the new spherulites were formed due to the crystallization of amorphous PLLA, as observed previously (Broz et al., 2003). 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 (Dell'Erba et al., 2001) 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 (Dell'Erba et al., 2001).

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 (Dell'Erba et al., 2001). 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 ( $T_g$ ) (IAEA-TECDOC-1420, 2004).

According to Michler (2008),  $\gamma$  or electron irradiation initiates pronounced crosslink in the amorphous parts of semi-crystalline polymers, whereas the structure inside the lamellae (the crystallinity) is not destroyed, so long as critical doses are not used. In this study, micrographs of PCL and PLLA homopolymers and PCL:PLLA 50:50 (w:w) blend irradiated with 100 kGy and 500 kGy, respectively, are shown in Figure 11 up to Figure 16.



Acceleration voltage: 20.0 kV Magnification: 2500

Fig. 11. Scanning electron micrographs of as extruded PCL, cryogenic fractured sample: A) non irradiated and B) irradiated with 100 kGy.

In Figure 12 it is possible to observe that lamellar structures increase on the fractured surface of PCL irradiated with 500 kGy, indicating that possibly significant crosslinking occurred.

Comparing the scanning electron micrographs, 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 15 wt %, indicating the enhance of crosslinking degree up to 200 kGy radiation dose (Södergard & Stolt, 2002). Even though PCL crosslinking predominates at radiation doses higher than 5 kGy and random chain-scission at lower doses (Södergard & Stolt, 2002; Ohrlander et al., 2000). In this chapter, only few changes could be seen by SEM for the irradiated PCL up to 100 kGy. However, 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 caused this alteration.

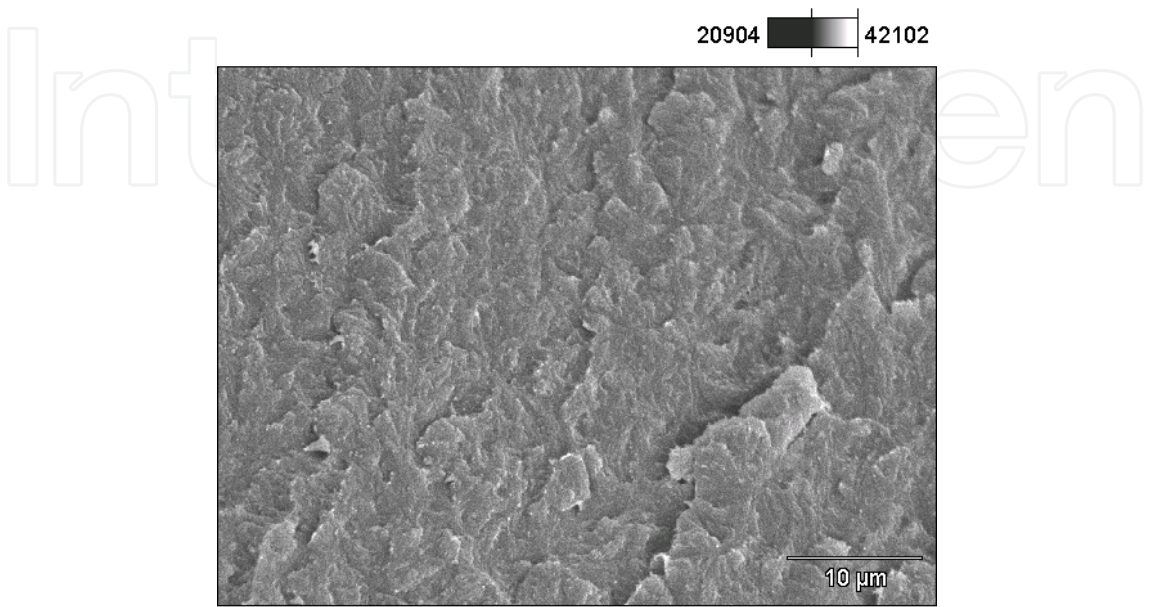
Some differences observed on micrographs A and B on Figure 13 probably are related to different regions analyzed. Apparently, an increase of granulation occurred on the polymeric matrix for 100 kGy irradiated sample.

Comparing Figures 13 and 14, some cracks appear, and polymeric surface seems to become smoother, probably due to significant scission of polymeric chains.

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 phase of the polymer (Södergard & Stolt, 2002). 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 (Nugroho et al., 2001). Apparently no

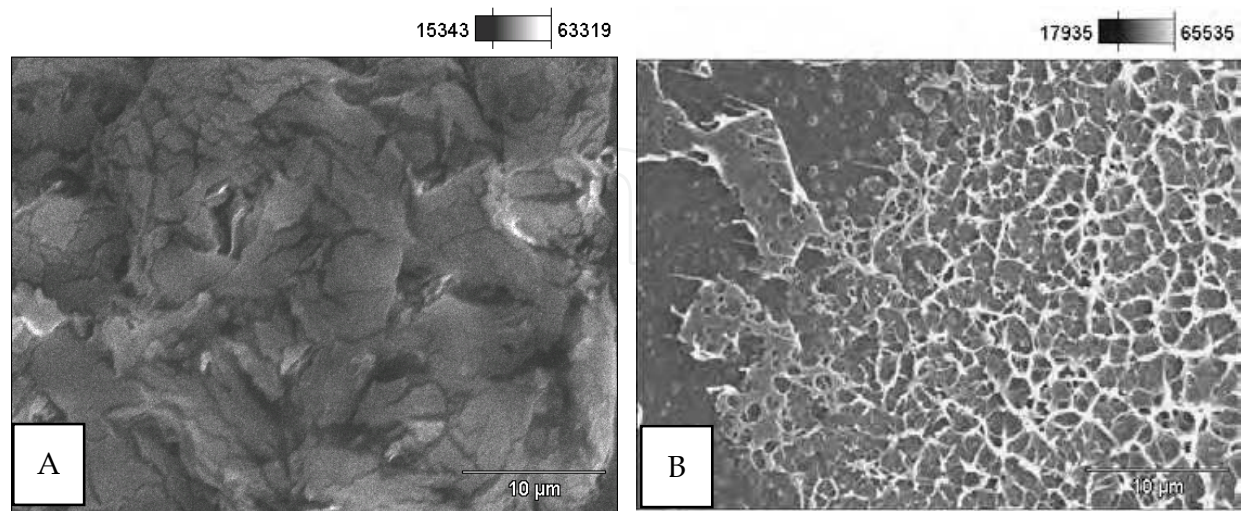


changes are visible by SEM on the irradiated PLLA with 500 kGy radiation dose, in contrast to other properties observed previously in the literature (Södergard & Stolt, 2002; Ohrlander et al., 2000; Nugroho et al., 2001).



Acceleration voltage: 10.0 kV Magnification: 2000×

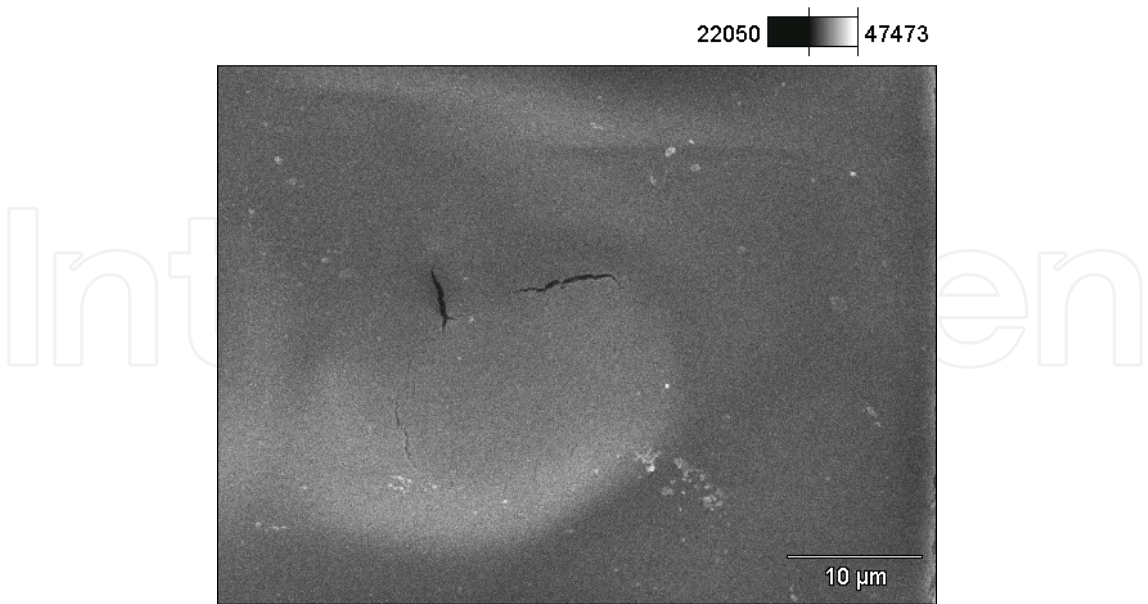
Fig. 12. Scanning electron micrograph of as extruded PCL, cryogenic fractured sample irradiated with 500 kGy.



Acceleration voltage: 20.0 kV Magnification: 2500×

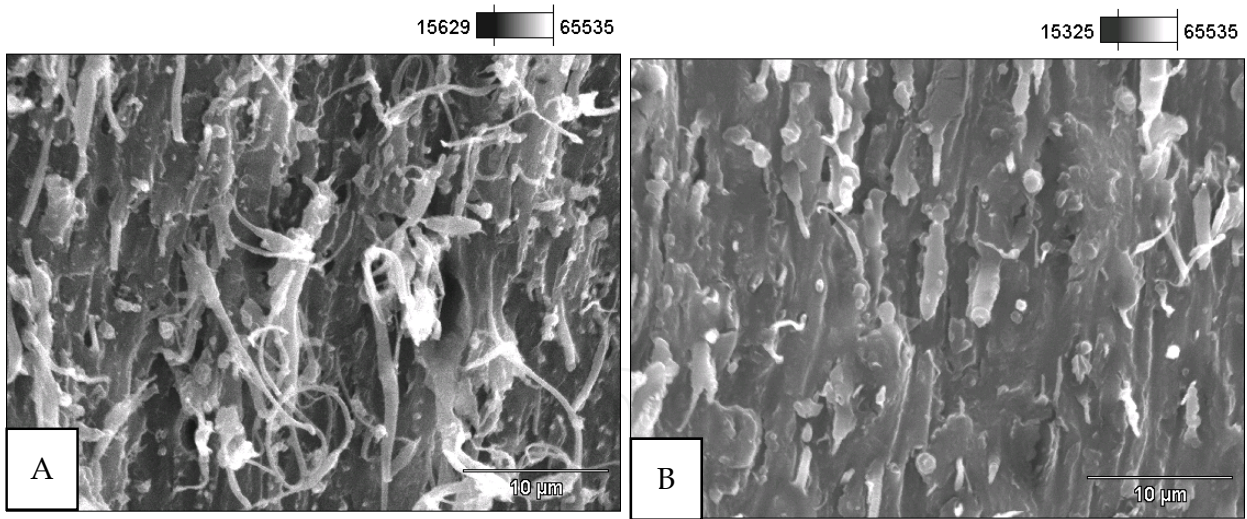
Fig. 13. Scanning electron micrographs of as extruded PLLA, cryogenic fractured sample: A) non irradiated and B) irradiated with 100 kGy.





Acceleration voltage: 10.0 kV Magnification: 2000×

Fig. 14. Scanning electron micrograph of as extruded PLLA, cryogenic fractured sample irradiated with 500 kGy.

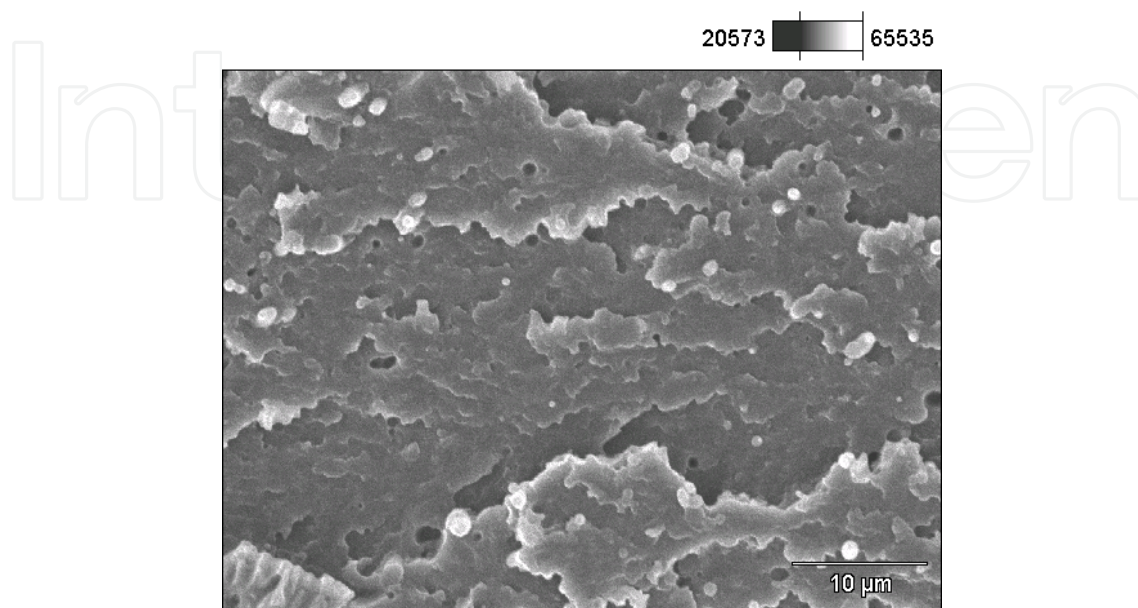


Acceleration voltage: 20.0 kV Magnification: 2500

Fig. 15. Scanning electron micrographs of as extruded PCL:PLLA 50:50 (w:w), cryogenic fractured sample: A) non irradiated and B) irradiated with 100 kGy.

Broz et al. (2003) observed that microstructure of PLLA 0.4 in PCL was characterized by relatively wide quantity of spherical inclusions of PLLA on PCL matrix. Particles had sizes varying from 5 μm to 100 μm, apparently isolated on the matrix. Similar micrograph was observed in Figure 15A. Irradiated blends micrographs, shown in Figures 15B and 16, suffered scales formation similar to that observed for irradiated PCL. The interface between

spherical inclusions and polymeric matrix seemed to be clean, suggesting that exists a weak adhesion between two phases, in consonance with absence of thermal transitions dislodgement observed by DSC. This lack of adhesion is unexpected since both polymers had been stated as miscible in the molten state.



Acceleration voltage: 10.0 kV Magnification: 2000××

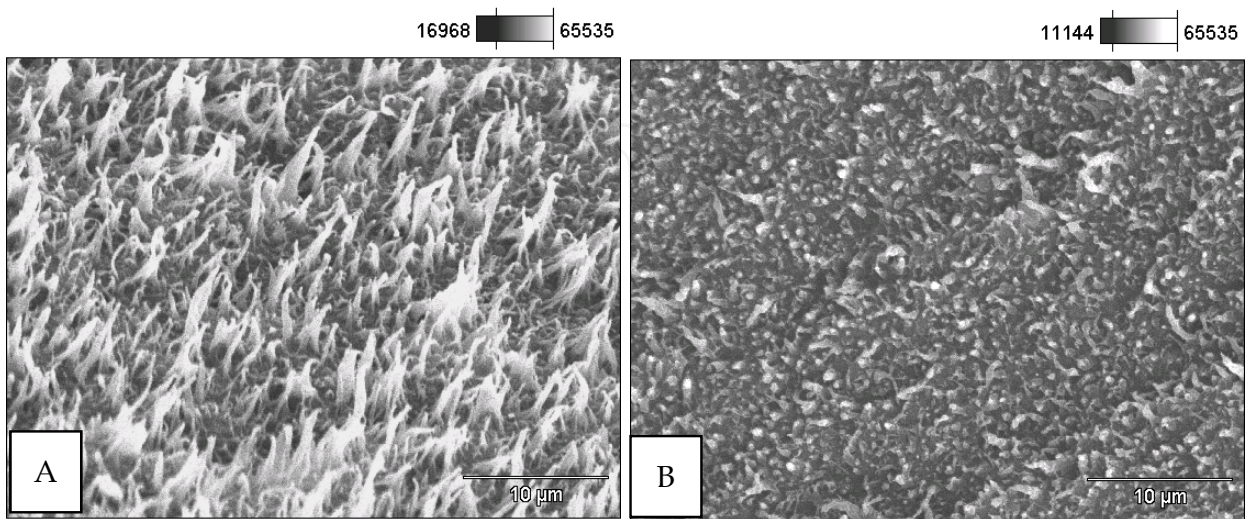
Fig. 16. Scanning electron micrograph of as extruded PCL:PLLA 50:50 (w:w), cryogenic fractured sample irradiated with 500 kGy.

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 bellow 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 (Kodama et al., 2005). On the other hand, after irradiation with higher doses, PCL samples were more thermally stable than PLLA and blend (Nugroho et al., 2001). Thermal properties of PLLA were not affected by gamma radiation up to 100 kGy (Kodama et al., 2006a). Other results obtained previously by Kodama et al.(2006b) 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 (Fourier Transform Infrared Spectroscopy). As well, the miscibility of the polymeric blends was not affected by the irradiation process (Kodama et al., 2006b).

It can be observed in Figure 17A and B that fractured surface of non irradiated blend presented several needles like structures orthogonal to the surface, apparently related to PCL, due to the



proportion of this component in the blend. Radiation dose seemed to induce these structures to diminish, probably related to PCL crosslinking that occurred with 100 kGy radiation dose.



Acceleration voltage: 20.0 kV Magnification: 2500×

Fig. 17. Scanning electron micrographs of as extruded PCL:PLLA 75:25 (w:w), cryogenic fractured sample: A) non irradiated and B) irradiated with 100 kGy.

Following micrographs were obtained using field emission scanning electron microscopy (FE-SEM) that dispense the use of Au<sup>0</sup> coating and energy for image obtaining is lower. Micrograph of PCL:PLLA 20:80 (w:w), non irradiated is shown in Figure 18. It was observed a rough surface.

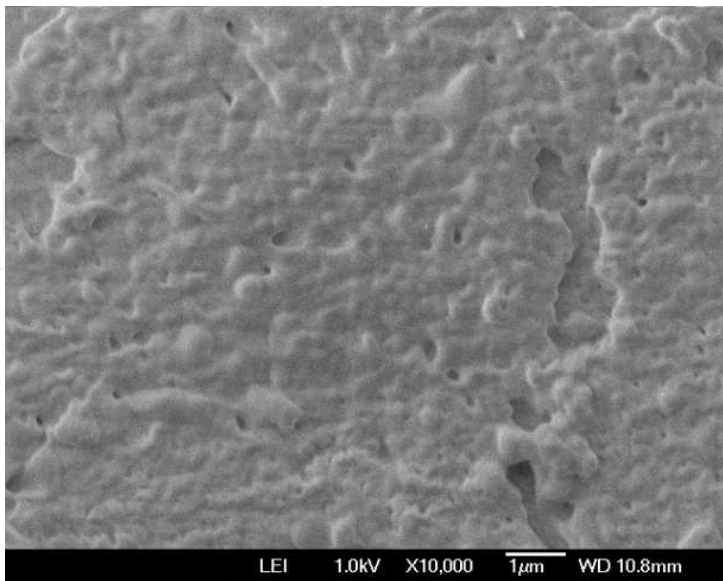


Fig. 18. Field emission scanning electron micrograph of as extruded PCL:PLLA 20:80 (w:w), cryogenic fractured sample, non irradiated.

In Figure 19 is observed surface micrographs of samples of PCL:PLLA 20:80 (w:w) prepared by hot press process , non irradiated and irradiated with 20 kGy radiation dose. This dose look as if do not affect significantly blend surface. Considering that conventional radiation dose for sterilization is 25 kGy, it is not expected that significant alteration occurs on the blend morphology sterilized by ionizing radiation.

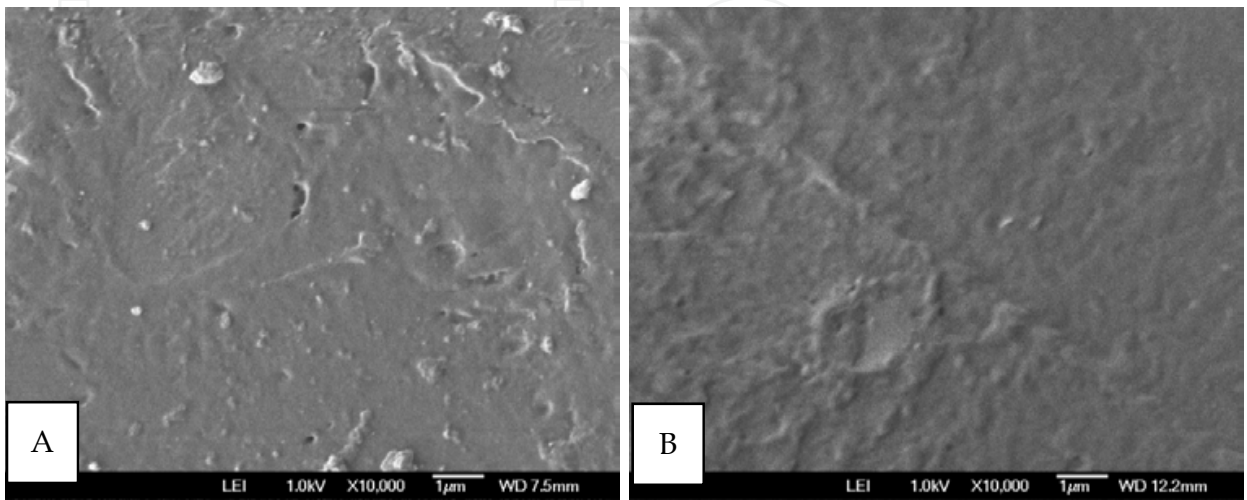


Fig. 19. Field emission scanning electron micrographs of hot pressed PCL:PLLA 20:80 (w:w) blends: A) non irradiated and B) irradiated with 20 kGy.

Arbelaiz et al. (2006) studied composites of linen fiber and PCL, and observed by SEM that fibers were clean and almost without adhesion points with PCL polymeric matrix, that indicated low wettability of fibers and lack of adhesion between phases. In Figure 20 it was no possible to observe in this sample regions containing fibers as observed by the authors mentioned before, probably it is related to its low concentration on the composite (5 or 10%) studied in this chapter. It was just observed what looks like a fragment of fiber.

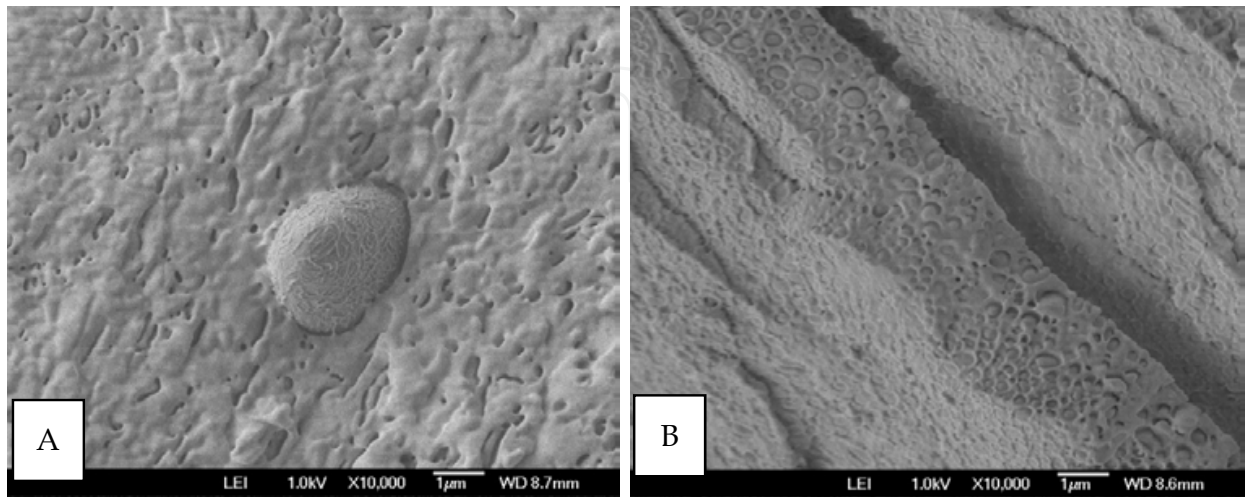


Fig. 20. Field emission scanning electron micrographs of composite with 10% non chemically treated coconut fiber: A) non irradiated; B) irradiated with 100 kGy, cryogenic fractured.



It was not possible to observe in Figure 21 significant alteration between structure existent and blend matrix. Apparently, acetylating process was not effective referring to the adhesion. However, it seems that ellipsoidal structures apart from polymeric matrix increased. Visually, structures suffered elongation and size reduction. Irradiated sample have smoother surface, probably related to scission process prevail of PLLA with doses above 100 kGy.

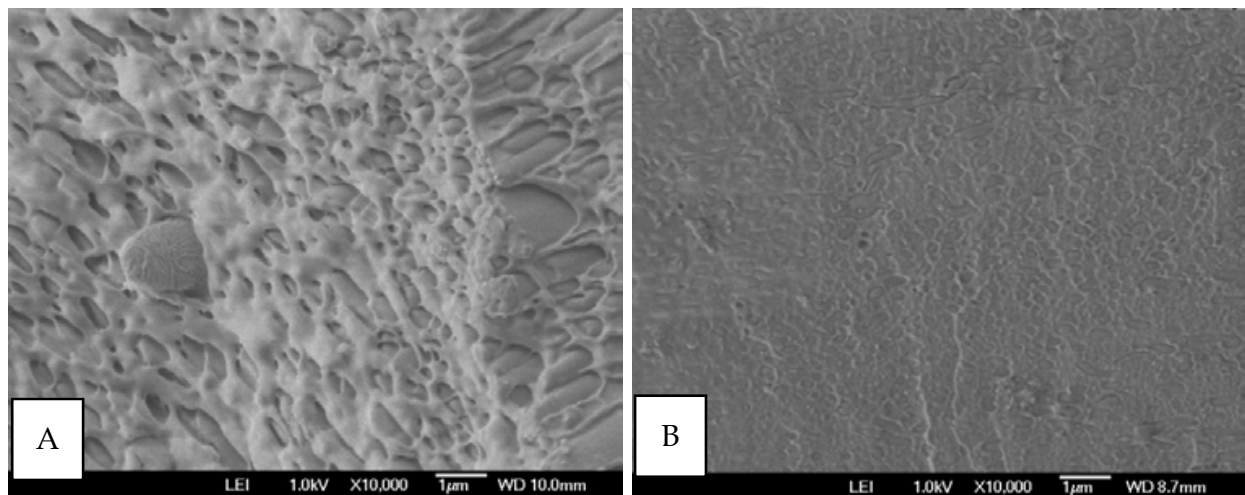
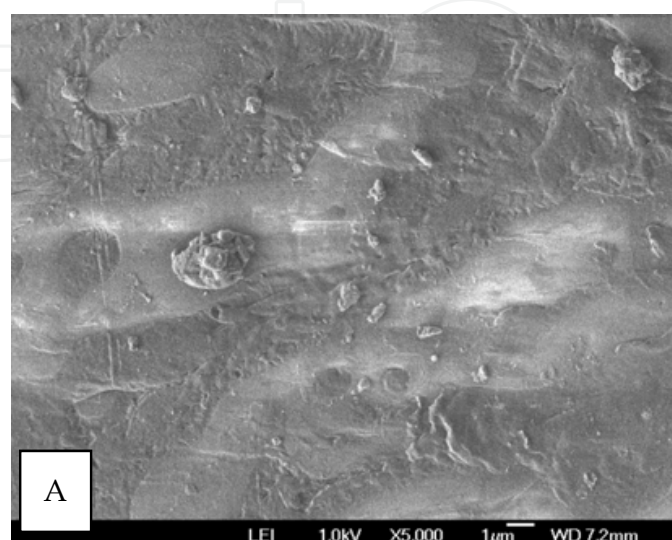


Fig. 21. Field emission scanning electron micrographs of composite with 10% acetylated coconut fiber: A) non irradiated; B) irradiated with 100 kGy, cryogenic fractured.

Micrographs of hot pressed sheets surface of composites containing 10% non chemically treated coconut fiber, non irradiated, and EB irradiated with 50 kGy and 100 kGy radiation doses, respectively, are shown in Figure 21. It was not possible to observe fiber presence on the surface analyzed. Neither any significant alteration on the irradiated surface, in the dose range studied. It suggests that cryogenic fractured surfaces allows the observation of irradiation effect on the polymeric bulk that otherwise could not be observed on sample surface. Probably it occurs due to the fact that species formed by energy deposition of radiation through polymeric matrix reacts mainly on the bulk than on the surface.



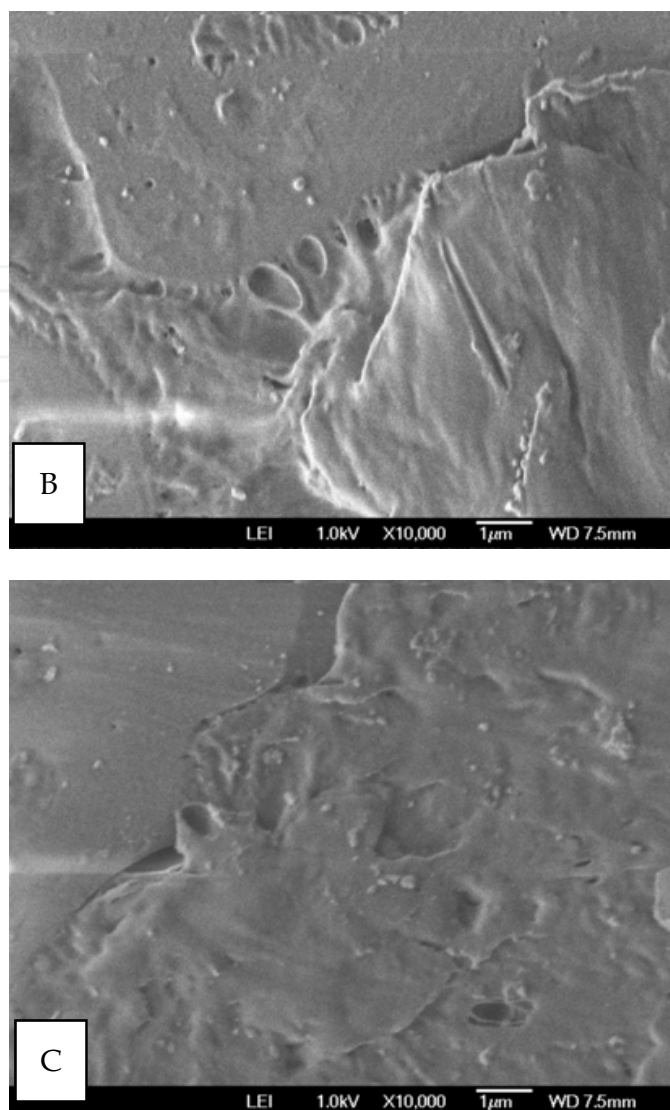


Fig. 22. Field emission scanning electron micrograph surface of hot pressed sheet of composite containing 10% non chemically treated coconut fiber: A) non irradiated; B) EB irradiated with 50 kGy, and C) EB irradiated with 100 kGy.

#### 4. Conclusion

Due to coalescence effect it was possible to observe spherical inclusions of PLLA in PCL:PLLA blend. Increasing radiation dose induced elongation of inclusions, as well, lamellar structures increase in the PCL matrix. Radiation doses higher than 100 kGy altered morphologies of samples surfaces, that became smoother, attributed to the presence of smaller fractions of PLLA, as a result of long chain scission, and high crosslinking reaction in PCL phase. Radiation processing and chemical acetylating did not promote measurable interaction between fibers with polymeric matrix.

The SEM micrographs of the fractured homopolymers and blends have shown their immiscibility. The crystallization of PLLA could be observed on the annealed samples. Samples irradiated with 100 kGy presented little variation on the morphology, even

supposing that the structural modifications induced by ionizing radiation may alter the morphology of the samples. 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. It was also studied blends and composites based on PCL, PLLA, and coconut fiber. Acetylation of fibers was not effective in order to induce any interaction between fibers and polymeric matrix, as expected. Ionizing radiation neither promoted detectable interaction between polymeric matrix and fibers.

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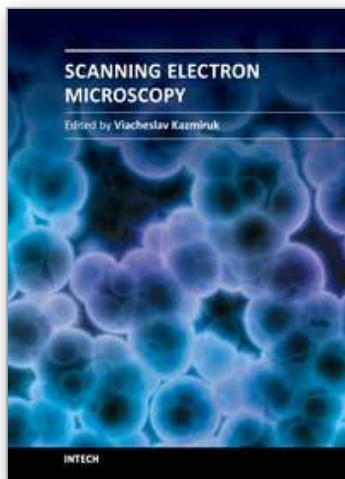
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## **Scanning Electron Microscopy**

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Today, an individual would be hard-pressed to find any science field that does not employ methods and instruments based on the use of fine focused electron and ion beams. Well instrumented and supplemented with advanced methods and techniques, SEMs provide possibilities not only of surface imaging but quantitative measurement of object topologies, local electrophysical characteristics of semiconductor structures and performing elemental analysis. Moreover, a fine focused e-beam is widely used for the creation of micro and nanostructures. The book's approach covers both theoretical and practical issues related to scanning electron microscopy. The book has 41 chapters, divided into six sections: Instrumentation, Methodology, Biology, Medicine, Material Science, Nanostructured Materials for Electronic Industry, Thin Films, Membranes, Ceramic, Geoscience, and Mineralogy. Each chapter, written by different authors, is a complete work which presupposes that readers have some background knowledge on the subject.

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