NUKLEONIKA 2013;58(4):459–468

ORIGINAL PAPER

Atomic force microscopy investigation of electron beam (EB) irradiated composites based on biodegradable polymers and coconut fiber*

Yasko Kodama, Akihiro Oishi, Naotsugu Nagasawa, Kazuo Nakayama, Masao Tamada, Luci D. B. Machado

Abstract. In this study, the addition of natural fibers to biodegradable PCL, PLLA blend and the effect of ionizing radiation on the surface of composites were investigated by force modulation microscopy (FMM), atomic force microscopy (AFM) and scanning electron microscopy (SEM). Hot pressed sheets were prepared using pellets of twin extruded PCL:PLLA 20:80 (w:w) blend containing 5% or 10% weight concentration of coconut fiber. In this study coconut fibers non treated chemically and acetylated ones were used. Irradiation was performed using an electron beam (EB) accelerator and an absorbed dose of 100 kGy. FMM images acquisition was obtained using a silicon cantilever, intermittent contact mode (tapping mode). Also, AFM images were obtained using tapping mode but J scanner. By FMM, it was possible to observe regions with different elasticity indicating fiber presence under the surface of the composite. Furthermore, it appears that the spherical structures size decreased on composites. This probably was induced by ionizing radiation.

Key words: atomic force microscopy (AFM) • coconut fiber • electron beam (EB) radiation • force modulation microscopy (FMM) • poly(ε-caprolactone) (PCL) • poly(L-lactic acid) (PLLA) • scanning electron microscopy (SEM)

Y. Kodama✉, L. D. B. Machado
Nuclear and Energy Research Institute (IPEN-CNEN/SP),
Radiation Technology Center,
2242 Prof. Lineu Prestes Ave.,
05508-000, São Paulo, Brazil,
Tel.: +55 11 3133 9816, Fax: +55 11 3133 9765,
E-mail: ykodama@ipen.br

A. Oishi, K. Nakayama
National Institute of Advanced Industrial Science and Technology (AIST),
Research Institute for Innovation in Sustainable Chemistry, Central 5,
1-1-1 Higashi, Tsukuba-city, Ibaraki-ken, 305-8565, Japan

N. Nagasawa, M. Tamada
Japan Atomic Energy Agency (JAEA),
Quantum Beam Science Directorate,
1233, Watanuki-machi, Takasaki, Gunma-ken, 370-1292, Japan

Received: 5 March 2012
Accepted: 1 October 2012

Introduction

The problem of environmental pollution caused by plastic waste can be solved by the development of biodegradable polymeric materials [17]. 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 [2, 6, 7, 10]. The controlled degradation of polymers is sometimes desired for biomedical applications and environmental purposes. PLLA is a hard, transparent and crystalline polymer [15]. 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 [7]. 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 [14], usually different polymers are incompatible. Improved properties can be only realized if the blend exhibits optimum morphology. According to Sawyer [21], in polymer science, the term morphology generally refers to form and organization on a size

*Presented at the International Meeting on Radiation Processing, IMRP 2011, 13–16 June 2011, Montreal, Canada.

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 [6]. 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 [2, 4, 8]. 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. Enzymatic and non-enzymatic degradations occur easier in the amorphous region [13, 23]. Kikkawa *et al*. [10] 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*. [16] 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 economical 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 coconut fiber, is composed of cellulose and lignin, which suffers chemical alteration by irradiation such as scission or crosslinking. In the case of natural polymers, like cellulose, main chain scission occurs predominantly due to irradiation and as a result molecular weight decreases [4].

The structures and morphologies of polymers have been under investigation for more than 60 years. Atomic force microscopy (AFM), has become a technique extensively used to a wide range of applications. Due to its capacity of acquiring information that are not possible to obtain by scanning electron microscopy (SEM), it has been used to study polymers in a large extent. For instance, by using AFM, it is possible to measure directly height and roughness of the investigated structures and furthermore, topographic images of ordered structures with atomic resolution. Those images can be obtained by means of a probe that scans sample surface, and changes within the material and may be analyzed by observing the sample cross-section obtained by freeze--fracturing in liquid nitrogen [2, 3, 18]. Force modulation microscopy (FMM) mode is an extension of AFM that includes mechanical properties characterization of the sample surface. FMM is especially interesting to study composites and materials with different elasticity regions, so contrast of the images is related to the local rigidity of the polymer [3, 24, 26]. Semba *et al*. [22] mentioned that poly(lactic acid) (PLA) resin as a bio-based polymer is expected to become a "green substitute" for petroleum-based polymers in commodity and perhaps engineering applications. But it has defects such as brittle properties, low heat resistance, and poor processing properties. Recently, some authors improved this brittle nature by blending with polycaprolactone (PCL) and dicumyl peroxide (DCP). They cited that ductile nature of PCL gets imparted to the PLA matrix because of improved interfacial adhesion resulting from cocrosslinking formation by the DCP. This yielded a ductile material with five times better elongation at break than the corresponding blend without peroxide. In an analogous way, ionizing radiation produces polymeric radicals that would recombine and improve interfacial adhesion of PLLA and PCL blends. Furthermore, in the case of polymeric main chain scission predominance or radicals' reaction with oxygen from air, some degradation due to ionizing radiation might occur. Degradation of a biomaterial can also occur at different stages of its preparation, including its storage [2]. Khandwekar *et al*. [9] cited that many surface modification strategies that are designed for non-biodegradable polymers require surface activation, mainly preoxidation or irradiation. However, for biodegradable polymers, such changes may induce degradation and thus deteriorate the mechanical properties or even tissue compatibility. Then, it was expected that irradiated sample surfaces topography present some variation. Xu *et al*. [25] cited that for natural fibers comprising mostly of cellulose – a highly hydrophilic macromolecule with a strong polarity, problems of compatibility with very apolar matrices would arise. Surface treatments, although having a negative impact on economics, may improve the compatibility and strengthen the interface in natural fiber composite materials. For this reason, in this study we acetylated coconut fibers trying to improve their compatibility with a polymeric matrix of the blend. So, the influence of coconut fiber incorporation and ionizing radiation to PCL:PLLA 20:80 blends topography were investigated here.

In this paper, non-irradiated and EB irradiated composites of PCL:PLLA 20:80 (w:w) blend and coconut fiber were studied using AFM, FMM and SEM. The objective of this study was to observe the influence of natural fiber addition to the polymeric matrix, also the effect of ionizing radiation on the miscibility of both polymers and with coconut fiber. Furthermore, it was intended to observe the influence of chemical treatment on the interaction between them.

Experimental

Preparation of composite sheets

Coconut fiber

Coconut fibers were received from Embrapa, Paraipaba region, Ceará. Their size reduction was achieved by using a helix Marconi mill, 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 separation was done by using sieves of the Tyler series 16, 20, 35 and 48, fiber sizes of 1.0, 0.84, 0.417 and 0.297 mm, respectively. The sieve shaker Produtest was used during 1 min for the separation of triturated material. For the assays of this study, it was used a 0.417 mm fiber size.

Fiber acetylation was performed as described by D'Almeida *et al*. [5]. Pristine fibers of Embrapa were soaked in a solution of acetic anhydrate and acetic acid (1.5:1.0, w:w). It was used as a catalyst, 20 drops of sulfuric acid in 500 mL solution. Set were submitted to ultrasound for 3 h, then for next 24 h of rest at the same solution. Fibers were washed using tap water and leaved for next 24 h in deionized water. Fibers were separated from water and washed with acetone, after that, were evaporated at room temperature.

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, $M_w = 2.64 \times 10^5$ g·mol^{-1} $\bar{M}_w / \bar{M}_n = 1.518$ – Gel Permeation Chromatographic values) and dry 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 PLLA:PCL 80:20 (w:w) blend and composites containing 5 and 10% (w:w) of untreated and chemically treated coconut fiber were prepared at AIST.

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

Electron beam irradiation

Irradiation was performed at JAEA using an electron beam accelerator (2 MeV; 2 mA), the absorbed dose being 100 kGy and dose rate 0.6 kGy·s^{-1}. The energy and current parameters condition of irradiation was enough for the electron beam to go through sheets of 0.5 mm thickness. Surfaces of the non-irradiated and irradiated samples of compressed sheets were studied by FMM and the surfaces of cryogenic fractured samples were analyzed by AFM.

Modulated force microscopy (MFM)

In FMM mode the AFM tip scans the sample in contact with the surface, applying oscillate force on the cantilever in a way that the tip slightly indents the surface, testing the elasticity. The tip will deform more the regions with a higher elasticity (less rigid) than the rigid regions. Therefore, the cantilever deflection will be inversely proportional to the local surface deformation of contact between the tip and the sample. Then, the relative elasticity through the sample surface is obtained recording the cantilever deflection amplitude in function of scan position on the surface. Regions with the higher elasticity appear clearer than the rigid regions. A silicon cantilever was used, tapping mode (intermittent contact mode), frequency = 265.4 kHz; tip radius = 15 nm (nominal); 512 points by line (512 × 512), scan size = 50 μm^2; integral gain = 0.5; peak-valley = 300 nm.

AFM – tapping mode

The J scanner was used. Non-irradiated sample images were obtained at z = 500 nm; lowpass; integral gain of 0.2; proportional gain of 5; amplitude of 1.627 V; drive frequency = 230.760 kHz. For the scan angle of 90°: scan rate = 1.0 Hz; integral gain = 2.483; proportional gain = 6.0; amplitude = 1.40 V; 100 nm (image saturated), it was altered to 150 nm.

The irradiated sample images were obtained with low resolution (128) 5 μm; 2 μm; z = 300 nm and 400 nm; scan size = 600 nm^2; z = 150 nm; amplitude = 1.30 V; integral gain = 0.25; proportional gain = 4.00; drive frequency = 230.766 kHz; amplitude = 0.5 V; retrace mode.

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.

Results and discussion

AFM surface images of hot pressed sheets (non-cryogenic fractured samples) non-irradiated and irradiated composites containing coconut fibers are shown in Fig. 1. It was possible to observe that the compressed sample surfaces topography variation is less than 500 nm for non-irradiated samples and it was not possible to observe coconut fiber on the surface of those images using AFM. In Fig. 1b, it can possible be seen white spots with structures higher than 500 nm, it seems that ionizing radiation induced some changes on the topography.

Kikkawa *et al*. [10] and Semba *et al*. [22] observed phase separated morphology attributed to polymeric blend immiscibility with two different contrast domains. The authors attributed to the brighter domain to PLLA that was the harder one. Semba *et al*. [22] observed PCL dark islands dispersed in the bright polylactic acid, PLA, sea, in which image contrast described stiffness and viscoelasticity of the components. In our study, it was possible to observe the immiscibility of both polymers. Even though PLLA is the preponderant component of the blend, the contrast observed on the image seems not to show this ratio, where brighter domain should be PLLA phase (harder phase), it suggests that in the phase image used here affected the image obtained, as cited by Wang *et al*. [24]. Besides that, in the experiment of Semba *et al*. [22], the cross-sectional area was adjusted to a flat surface by using a microtome equipped with a glass knife. In our study, we analyzed directly the surface of the prepared sheets by hot press the pellets and compressed cooling down, it is likely

that the difference between other author's and our research results should be because of the fast cooling process during compressing molding. As PCL possesses low glass transition and melting temperatures and, PLLA high melting temperature, as extruded PLLA is predominantly amorphous as observed previously [12]. Wang *et al*. [24] cited that the contradictory results have been reported based on a "composition correlation" method. While some attributed the brighter domains to hard areas, others assigned brighter domains in the phase image to soft materials. Zeng *et al*. [26] studied the influence of polymer crystallinity on the AFM images and observed that the higher modulus crystalline material appears brighter in the phase image and the softer, amorphous matrix appears darker.

In our previous study [11] we observed that there were no variations on the melting peaks or glass transition temperature varying blends composition indicating that the blends were immiscible. Furthermore, the miscibility of the polymeric blends was not affected by the irradiation process. In the literature, it was published that the thermal treatment induces PLLA melting temperature variation on irradiated blends with high concentration of PLLA. In this study it was not possible to observe separated phase differences neither due to PCL nor to PLLA as observed in PLA/polyhydroxybutyrate, PHB, blends by Kikkawa *et al*. [10], maybe due to a lower scan size used by them. Kuo [13] has cited that to enhance the formation of single-phase, miscible polymer blends, it is necessary to ensure that favor-

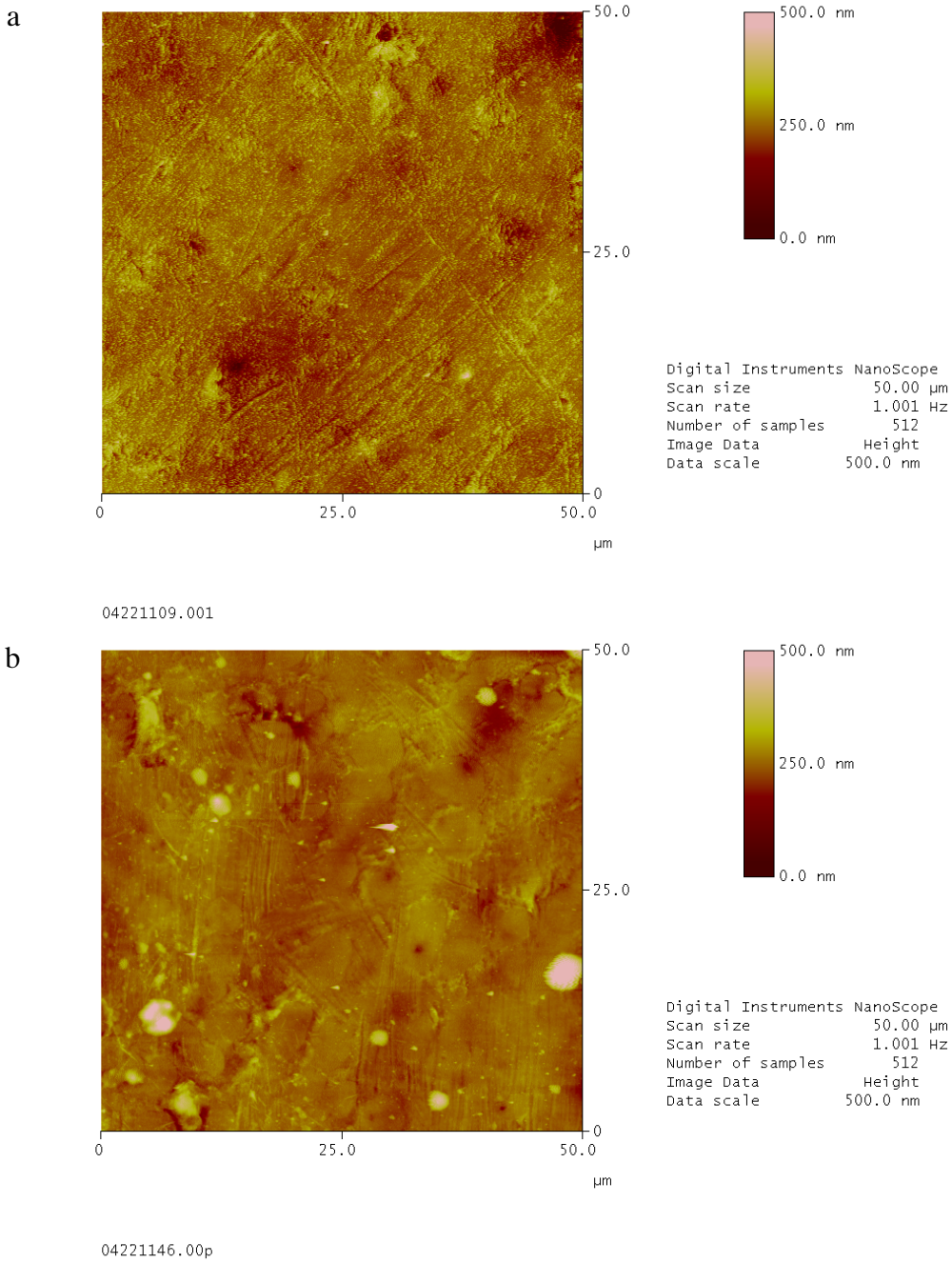

Fig. 1. AFM image of surface of PCL:PLLA 20:80 containing 5% of untreated coconut fiber: (a) non-irradiated; (b) EB irradiated with 100 kGy.

able specific intermolecular interactions exist between the two basic components of the blend.

Force modulated microscopy (FMM)

In addition to the topographic imaging, the phase imaging mode of AFM takes an active part in the mapping of surface heterogeneity of the blends because the phase response of the cantilever is sensitive to the surface characteristics, such as viscoelasticity, and the phase image contrast is dependent on the chemical and mechanical properties of the samples [10].

The images of non-irradiated composite containing 10% of untreated coconut fiber, obtained by AFM and FMM, are shown in Figs. 2a and 2b. While the AFM image shows the topography irregularity, the FMM generates a force modulation image, which is a map of the sample's elastic properties, from the changes in the amplitude of cantilever modulation.

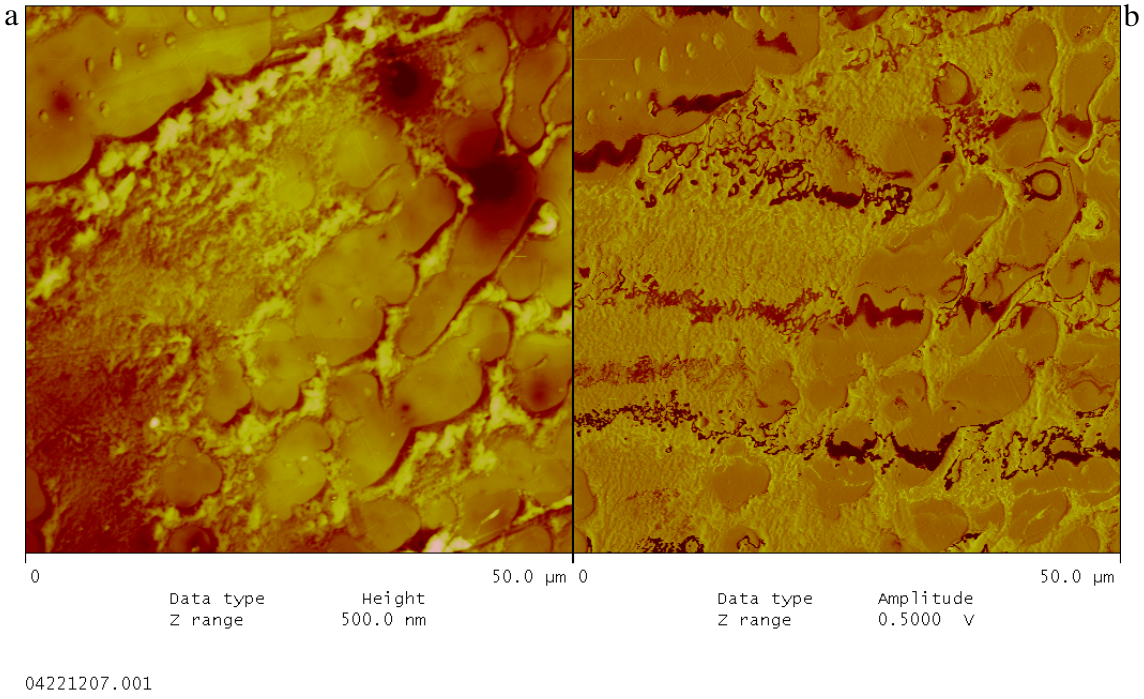

Fig. 2. Images of surface of non-irradiated PCL:PLLA 20:80 containing 10% of untreated coconut fiber: (a) AFM, height 500 nm; (b) FMM, amplitude 0.5 V.

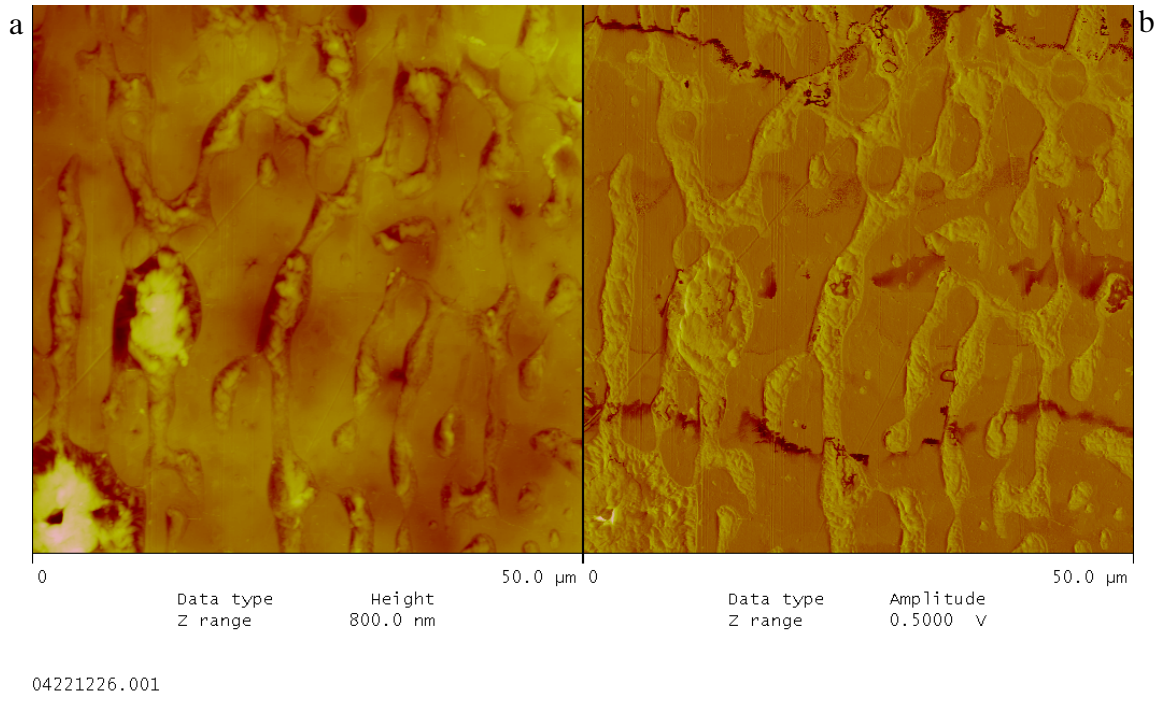

Fig. 3. Images of surface of 100 kGy EB irradiated PCL:PLLA 20:80 containing 10% of untreated coconut fiber: (a) AFM, height 800 nm; (b) FMM, amplitude 0.5 V.

The images of 100 kGy EB irradiated composite containing 10% of fiber, obtained by AFM and FMM, are shown in Figs. 3a and 3b, respectively. Analogous to the previous figure, the intermittent contact of (a) images obtained by AFM, it is possible to observe heigh differences in the topography of surface, and changes of amplitude observed by FMM show the difference in hardness due to fiber presence under the surface.

Comparing (a) and (b) micrographs of Figs. 2 and 3, it is possible to observe regions that contain different elasticity, in which the darker ones observed in FMM images present a higher rigidity indicating fiber presence very close to the sample surface, affecting elastic properties of the sample. Even though, the fiber was not observed on the analyzed surface by AFM, using FMM technique which permitted to observe differences in hardness due to fiber presence under the surface.

AFM tapping mode

Images of N_{2liq} fractured surface of non-irradiated composite containing 10% of untreated fiber are shown in Fig. 4. It is possible to observe spherical structures on

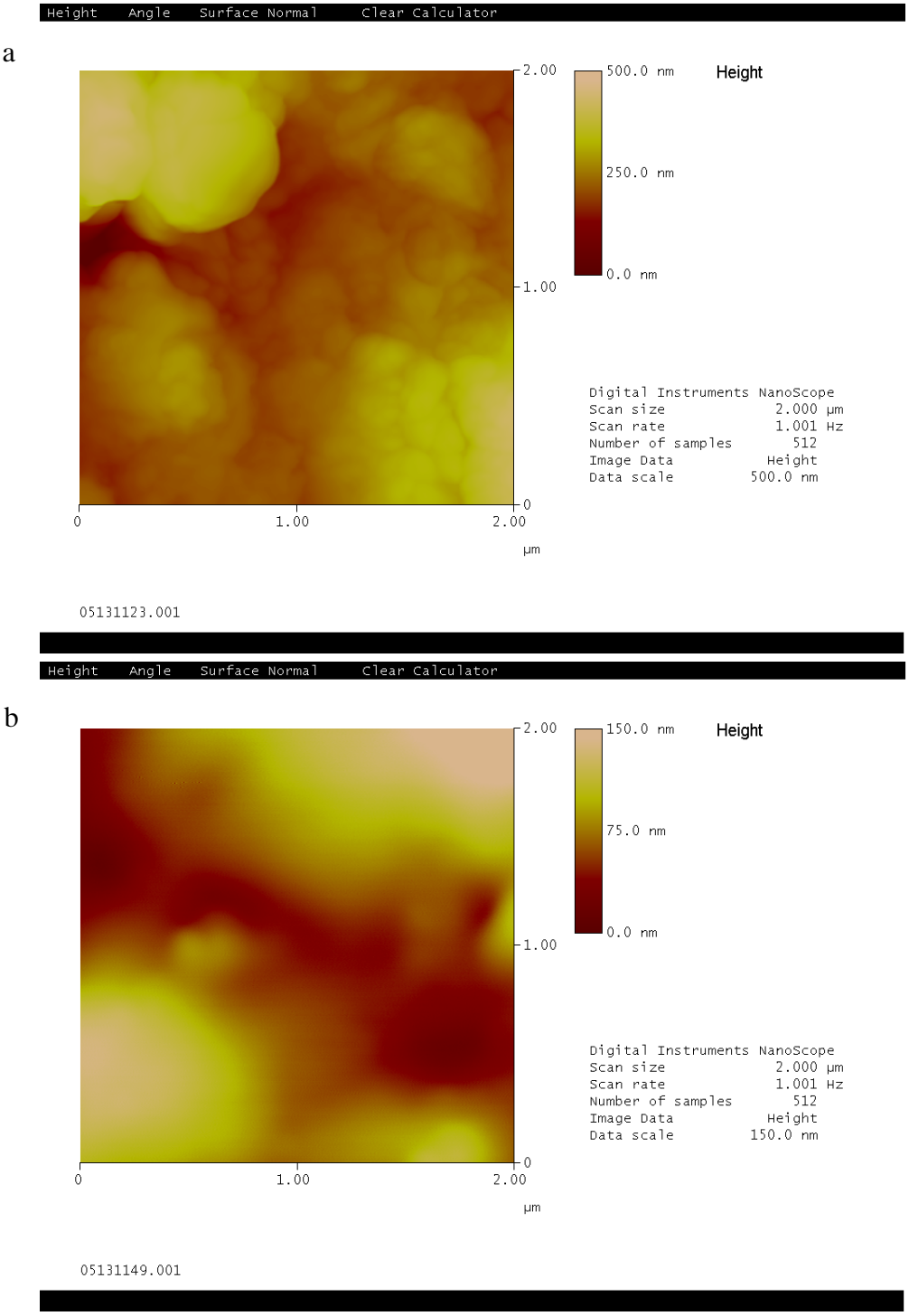

Fig. 4. AFM image (tapping mode) of N_{2liq} fractured non-irradiated PCL:PLLA 20:80 containing 10% of untreated coconut fiber: (a) z = 500 nm; (b) z = 150 nm.

the irregular surface, but it was not possible to visualize fiber presence. Khandwekar *et al*. [9] studied, using AFM, contact mode, surfaces of PCL films prepared by solvent evaporation. The authors observed that the PCL surface was relatively smooth at atomic level.

In order to evaluate the influence of chemical treatment of the fibers on the adhesion with polymeric matrix, images of non-irradiated composite containing 10% of acetylated fiber are shown in Figs. 5a and 5b. The spherical structures apparently suffered elongation, and this suggests that the treated fiber affected the original spherical polymeric structures.

The images of 100 kGy irradiated composite containing 10% of untreated fiber, are shown in Figs. 6a and 6b. It appears that the spherical structure size decreased, probably induced by ionizing radiation. Ražem, Katušin-Ražem [19] mentioned that large dose-rate (electron) irradiation of solid substances produces a large steady-state concentration of free radicals in a polymeric matrix which leads to an increased probability of mutual reactions between radicals situated on the same macromolecule (intramolecular crosslinking) that might explain the structural size decrease observed here. Nugroho *et al*. [17] observed that the average molecular weight of PLA decreased abruptly up to 200 kGy due to chain scission. Radicals at the polymer chain ends terminated by a chain transfer or hydrogen abstraction from neighboring polymer chains, and new radicals' production. An other reaction is the double bonds creation at chain ends after hydrogen release. The authors also observed that the melting peak of PLA became broader and shifted to lower temperatures with absorbed dose in-

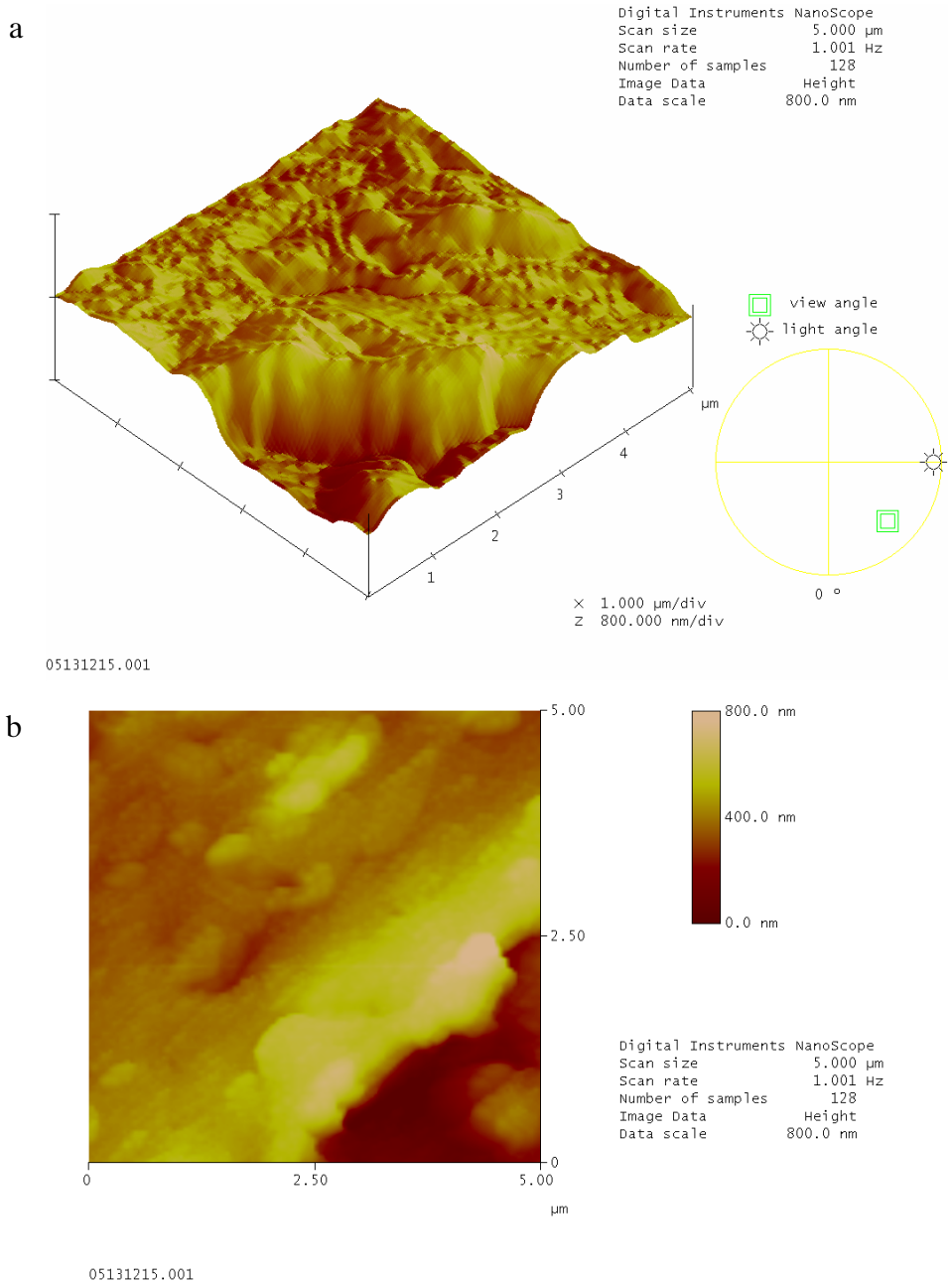

Fig. 5. AFM image tapping mode of N_{2liq} fractured non-irradiated PCL:PLLA 20:80 containing 10% of acetylated coconut fiber: (a) 3D image; (b) scan size 5 µm, z = 800 nm.

crease attributed to further degradation or introduction of irregularities from crystalline surfaces to the inside.

It was not possible to observe the presence of fibers in the studied regions, maybe due to their dispersion on the polymeric matrix of the samples studied here. It is important to keep in mind that the dimension of fibers are hundreds of micrometer and those of AFM images hundreds of nanometer.

Particles sizes from 50 nm up to 100 nm (irradiated samples) and 200 nm (non-irradiated samples) observed in this study were smaller than the ones observed by Sarazin *et al*. [20], that was 370–510 nm. Sarazin *et al*. studied ternary mixtures of PCL/PLA/glycerol starch. Probably the presence of glycerol in the authors' sample increased the coarsening effect that the coconut fiber presence did not cause in this study.

Arbelaiz *et al*. [1] studied composites of linen fiber and PCL and observed by SEM that fibers were clean and almost without adhesion points with a PCL polymeric matrix, that indicated low wettability of fibers and lack of adhesion between the phases. In Fig. 7, it is not possible to observe in this sample regions containing fibers as observed by the authors mentioned before, probably this is related to its low concentration of the composite (5 or 10%) studied here. It was just observed and looked like a fragment of fiber.

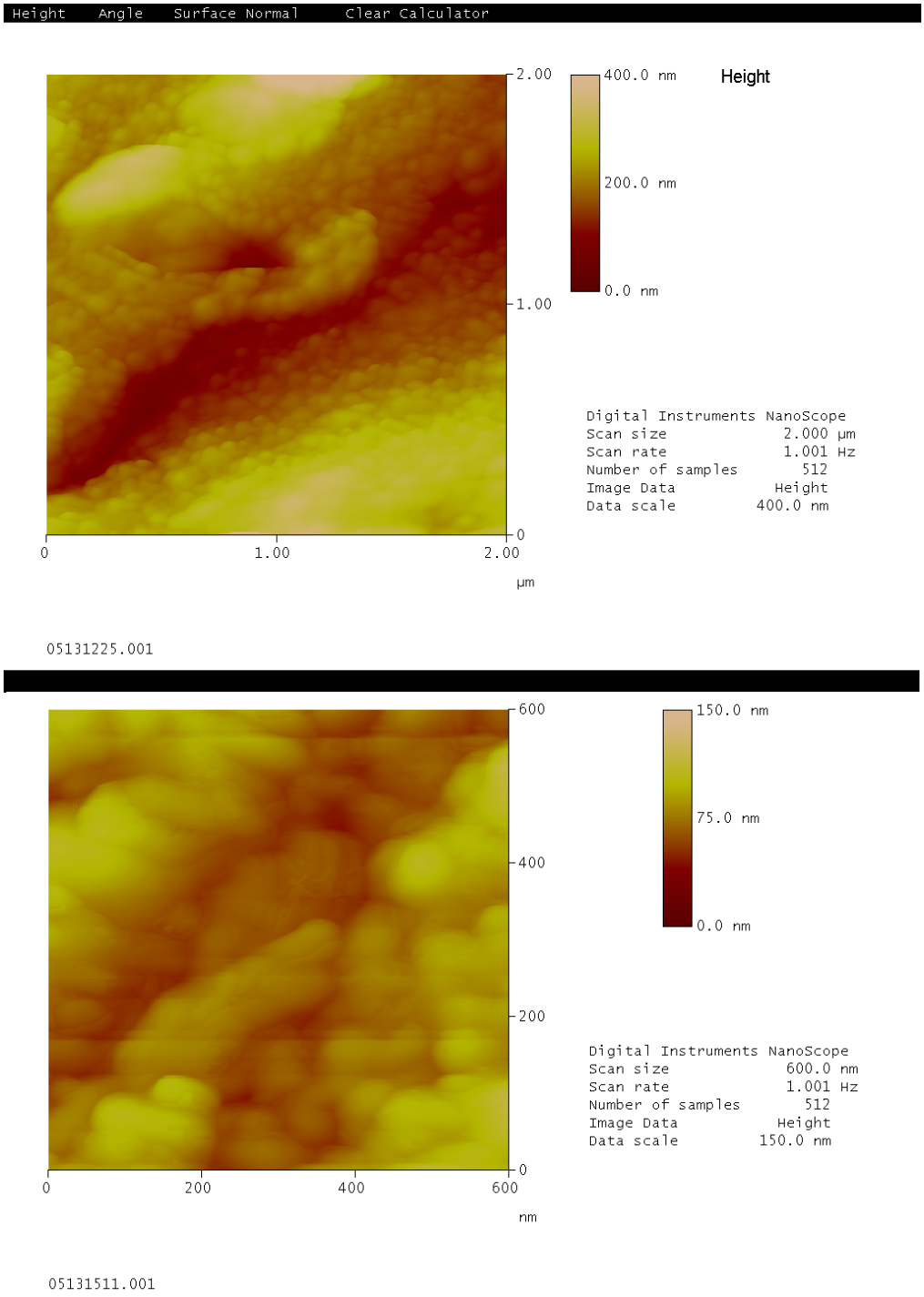

Fig. 6. AFM image (tapping mode) of N_{2liq} fractured PCL:PLLA 20:80 containing 10% of untreated coconut fiber sample, irradiated with 100 kGy: (a) z = 400 nm; (b) scan size = 600 nm, z = 150 nm.

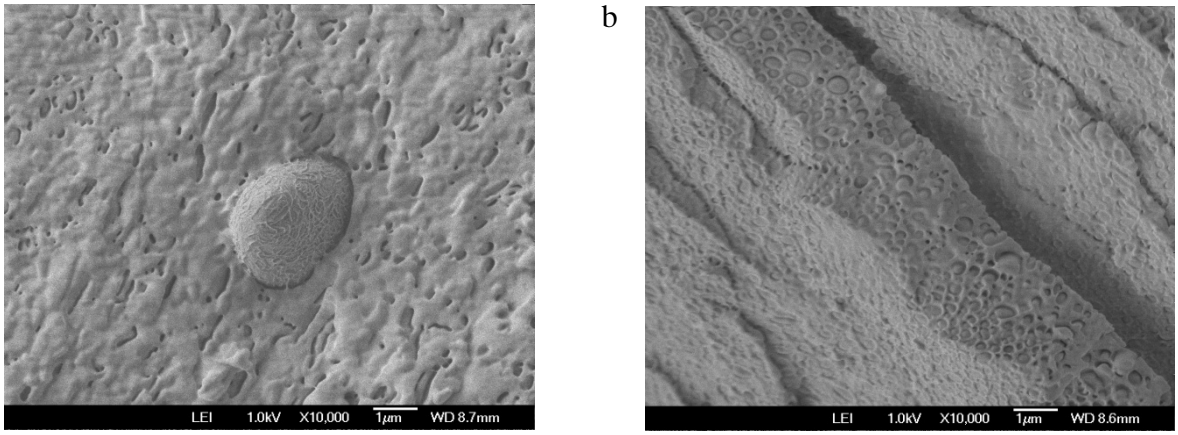

Fig. 7. SEM micrographs of composite with 10% non-chemically treated coconut fiber: (a) non-irradiated; (b) irradiated with 100 kGy, cryogenic fractured.

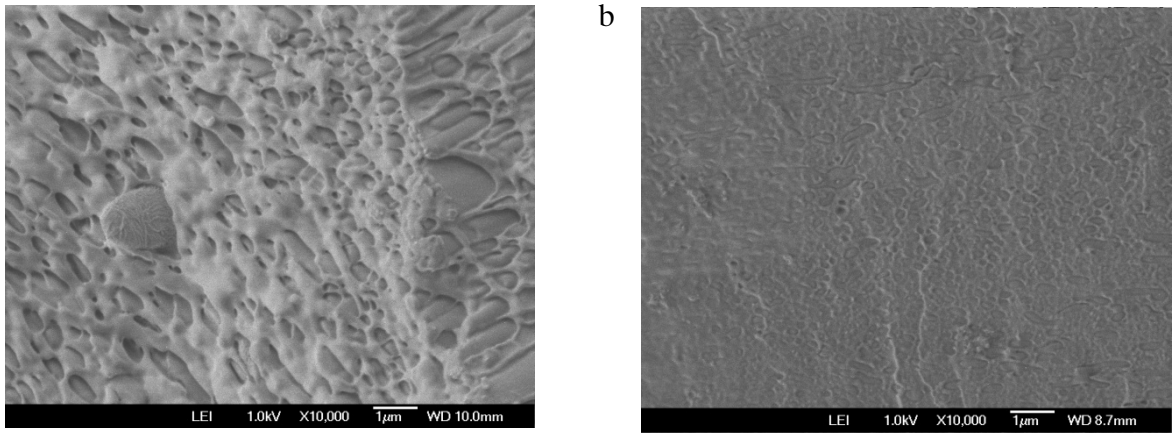

Fig. 8. SEM micrographs of composite with 10% acetylated coconut fiber: (a) non-irradiated; (b) irradiated with 100 kGy, cryogenic fractured.

It was not possible to observe in Fig. 8 significant alteration between the structure existent and the blend matrix. Apparently, the acetylating process was not effective referring to the adhesion. However, it seems that the ellipsoidal structures apart from the polymeric matrix increased. Visually, the structures suffered elongation and size reduction. The irradiated samples have a smoother surface, probably related to scission process prevailing over PLLA with doses above 100 kGy.

Conclusion

The AFM images of compressed biodegradable PLLA:PCL blend containing coconut fiber surfaces allowed us to observe that the topography variation is less than 500 nm for non-irradiated samples and some spots of structures higher than this value appear after irradiation. FMM allowed to observe regions with different elasticity, indicating fibers presence below the studied surface. It was possible to observe size decrease and elongation of spherical polymeric structures occurred probably induced by ionizing radiation and fiber chemical treatment that was not possible to be observed by others techniques in previous studies. Apparently, the acetylating process was not effective referring to the adhesion between the polymeric matrix and coconut fiber.

Acknowledgment. We are grateful to the financial support from the IAEA and from FAPESP (Proc. 2011/06316-4). Additionally, to the Laboratório de Filmes Finos do IFUSP for the SPM facility (FAPESP Proc. 95/5651-0).

References

1. Arbelaiz A, Fernández B, Valea A, Mondragon I (2006) Mechanical properties of short flax fibre bundle/poly(ε-caprolactone) composites: influence of matrix modification and fibre content. Carbohyd Polym 64;2:224–232
2. Azevedo HS, Reis RL (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, pp 177–197
3. Bernardes Filho R, Mattoso LHC (2004) Microscopia de força atômica. In: Canevarolo SV (ed) Técnicas de Caracterização de Polímeros. Artliber, São Paulo, pp 201–207
4. Chmielewski AG (2005) New trends in radiation processing of polymers. In: Proc of Int Nuclear Atlantic Conference. Encontro Nacional de Aplicações Nucleares, 28 August – 2 September 2005, Santos, SP, Brazil: ABEN, 7 p
5. D'Almeida ALFS, Calado V, Barreto DW (2005) Acetilação da fibra de bucha (Luffa cylindrica) Polímeros: Ciência e Tecnologia 15;1:59–62
6. Dell'Erba R, Groeninckx G, Maglio G, Malinconico M, Migliozzi A (2001) Immiscible polymer blends of semicrystalline biocompatible components: thermal properties

and phase morphology analysis of PLLA/PCL blends. Polymer 42:7831–7840
7. Kammer HW, 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, vol. 5, pp 132–160
8. Kantoğlu Ö, Güven O (2002) Radiation induced crystallinity damage in poly(L-lactic acid). Nucl Instrum Methods Phys Res B 197:259–264
9. Khandwekar AP, Patil DP, Shouche Y, Doble M (2011) Surface engineering of polycaprolactone by biomacromolecules and their blood compatibility. J Biomater Appl 26;2:227–252
10. Kikkawa Y, Suzuki T, Tsuge T, Kanesato M, Doi Y, Abe H (2006) Phase structure and enzymatic degradation of poly(L-lactide)/atactic poly(3-hydroxybutyrate) blends: an atomic force microscopy study. Biomacromolecules 7:1921–1928
11. Kodama Y, Machado LDB, Giovedi C, Nakayama K (2006a) FTIR investigation of irradiated biodegradable blends. In: 17° Congresso Brasileiro de Engenharia e Ciência dos Materiais – CBECIMAT, Foz do Iguaçu, PR, Brazil
12. Kodama Y, Machado LDB, Nakayama K (2006b) Effect of gamma rays on thermal properties of biodegradable aliphatic polyesters blends. In: V Congresso Brasileiro de Análise Térmica e Calorimetria, MG, Brazil, Brazilian Association of Thermal Analysis and Calorimetry – ABRATEC
13. Kuo SW (2008) Hydrogen-bonding in polymer blends. J Polym Res 15:459–486
14. Michler GH (ed) (2008) Electron microscopy of polymers. Springer, Berlin
15. Mochizuki M, Hirami M (1997) Structural effects on the biodegradation of aliphatic polyesters. Polym Adv Technol 8:203–209
16. Nishino T, Hirao K, Kotera M (2006) X-ray diffraction studies on stress transfer of kenaf reinforced poly(L-lactic acid) composite. Composites: Part A 37:2269–2273
17. Nugroho P, Mitomo H, Yoshii F, Kume T (2001) Degradation of poly(L-lactic acid) by γ-irradiation. Polym Degrad Stab 72:337–343
18. Radmacher M, Tillmann RW, Gaub HE (1993) Imaging viscoelasticity by force modulation with the atomic force microscope. Biophys J 64:735–742
19. Ražem D, Katušin-Ražem B (2008) The effects of irradiation on controlled drug delivery/controlled drug release systems. Radiat Phys Chem 77:288–344
20. Sarazin P, Li G, Orts WJ, Favis BD (2008) Binary and ternary blends of polylactide, polycaprolactone and thermoplastic starch. Polymer 49:599–609
21. Sawyer LC, Grubb DT (2008) Polymer microscopy, 3rd ed. Meyers GF (ed) Springer, New York
22. Semba T, Kitagawa K, Ishiaku US, Hamada H (2006) The effect of crosslinking on the mechanical properties of polylactic acid/polycaprolactone blends. J Appl Polymer Sci 101:1816–1825
23. Tsuji H, Ishizaka T (2001) Blends of aliphatic polyesters. VI. Lipase-catalyzed hydrolysis and visualized phase structure of biodegradable blends from poly(ε-caprolactone) and poly(L-lactide). Intern J Biol Macromol 29:83–89
24. Wang Y, Song R, Li Y, Shen J (2003) Understanding tapping-mode atomic force microscopy data on the surface of soft block copolymers. Surf Sci 530:136–148
25. Xu H, Wang L, Teng C, Yu M (2008) Biodegradable composites: ramie fibre reinforced PLLA-PCL composite prepared by *in situ* polymerization process. Polym Bull 61:663–670
26. Zeng C, Zhang NW, Ren J (2011) Recent progress in AFM studies of biodegradable poly(lactic acid) materials. Chin Sci Bull, doi: 10.1007/s11434-012-5052-z