ATOMIC FORCE MICROSCPOY INVESTIGATION OF EB IRRADIATED COMPOSITES BASED ON BIODEGRADABLE POLYMERS AND COCONUT FIBER

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Abstract

Biodegradable polymers have been extensively studied in order to minimize the environmental impact of plastic residue. And, the addition of natural fibers can lead to physical properties improvement and also can reduce cost. Additionally, being biocompatible it is necessary to sterilize to make possible its use in contact with human tissue. It is well known that the ionizing radiation is a powerful tool to perform the sterilization of several materials and medical devices. Components materials surface plays an important role on determining the useful properties of material item in a wide applications objects. This situation certainly pertain to organic materials and emphasizes the point of view that surface and interfaces characterization of high quality is necessary to the appropriate use and improvement of those materials. In this paper force modulation microscopy and atomic force microscopy were used to investigate the effect of ionizing radiation on the composites surface based on PCL, PLLA and coconut fiber. It was possible to observe regions with different elasticity indicating fiber presence under the surface of the composite. Also, it was possible to observe the polymeric structure change due to the ionizing radiation processing.

Keywords: Poly(L-lactic acid); poly(ε-caprolactone); coconut fiber; AFM; FMM; EB radiation.

1 Introduction

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 (Kammer & Kummerlowe, 1994; Dell'Erba et al., 2001). 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). 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). 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, polymeric structural changes such as scission and crosslinking are induced by radiation processing of polymers (Kantoğlu & Guven, 2002). Chemical structure influences the biodegradation of solid polymers. Enzymatic and non enzymatic degradations occur easier in the amorphous region (Mochizuki & Hirami, 1997; Yamamoto et al., 1997; Lee et al., 1997; Cai et al., 1996; Perego et al., 1996; Tsuji & Ishizaka, 2001). The morphology of the blends affects the thermo mechanical properties (Nakayama & Tanaka, 1997) as well as the biodegradation of the polymers.

Atomic force microscopy (AFM) has become a technique extensively used in 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. Some of the AFM advantages compared to SEM and electronic transmission microscopy is that vacuum and neither metal coating are required, there is possibility of directly measure structures height and roughness, and furthermore, topographic images of ordered structures with atomic resolution can be obtained by means of a probe that scans sample surface (Bernardes Filho et al., 2004; Radmacher, 1993). 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 (Salvadori, 2010; Bernardes Filho, 2004). In this paper, non irradiated and EB irradiated composites of PCL:PLLA 20:80 (w:w) blend and coconut fiber were studied using AFM and FMM.

2 Experimental

2.1 Preparation of composite sheets

Pellets of PCL:PLLA 20:80 (w:w) and coconut fiber with 5% and 10% amount were prepared using a twin screw extruder (Labo Plastomill Model 150C, Toyoseki, Japan). Plates of pellets were prepared using a Tokyo Ikeda hot press machine from Japan Atomic Energy Agency – JAEA, Takasaki, Japan. Irradiation was performed at JAEA using electron beam accelerator (2 MeV; 2 mA), radiation dose of 100 kGy, dose rate of 0.6 kGy s^{-1}. Surfaces of non irradiated and irradiated samples were studied by FMM and fractured in N_{2liq} surfaces were analyzed by AFM.

2.2 FMM – modulated force microscopy

It was used a silicon cantilever, tapping mode (intermittent contact mode), frequency of 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.

2.3 AFM –tapping mode

It was used J scanner, scan size of 2 × 2 μm^2 ; z = 500 nm; Lowpass; Integral gain of 0.2; proportional gain of 5; amplitude of 1.627 V; drive frequency = 230.760 kHz. For scan angle of 90º: 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.

Irradiated samples 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; phase in 2619; retrace mode.

3 Results and discussion

AFM images of non irradiated composites containing chemically untreated fibers are shown in Fig. 1, 2 and, 3. Imaging conditions of samples with 5% of fiber: scan size = 50 μm^2, z = 500 nm; samples with 10% of fiber: z=1000 nm; and, samples with 5% of fiber and irradiated with 100 kGy: z = 500 nm; respectively. Samples surfaces are flat and it was not possible to observe by AFM coconut fiber in the surface of those images.

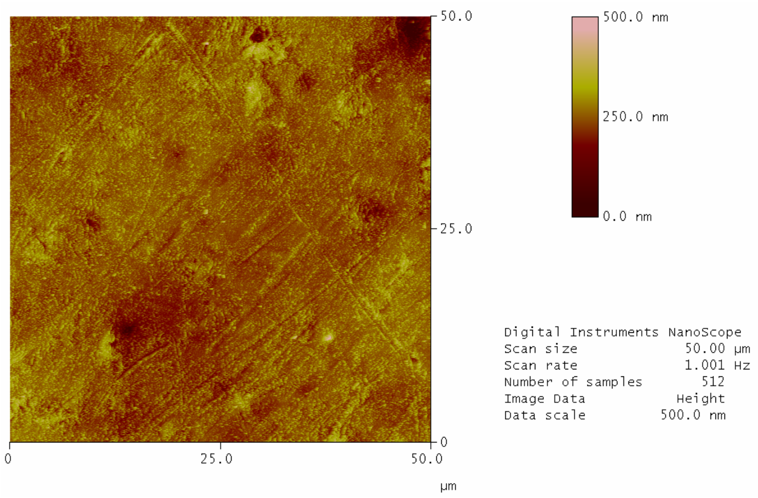


Fig. 1. AFM image of surface of non irradiated PCL:PLLA 20:80 containing 5% of untreated coconut fiber.

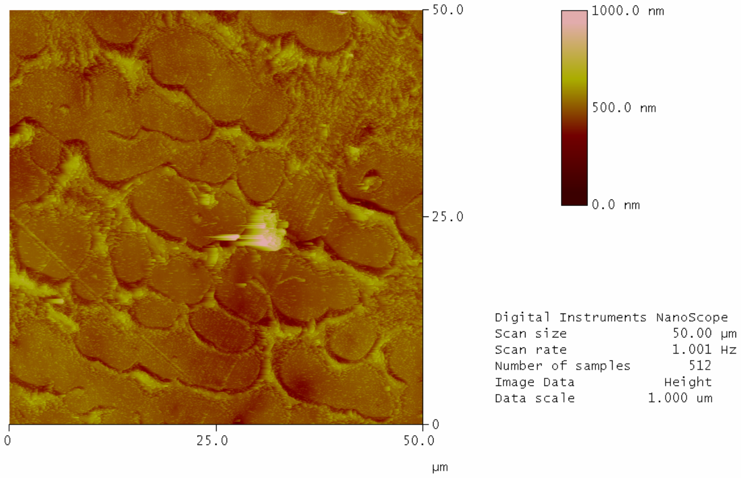


Fig. 2. AFM image of surface of non irradiated PCL:PLLA 20:80 containing 10% of untreated coconut fiber .

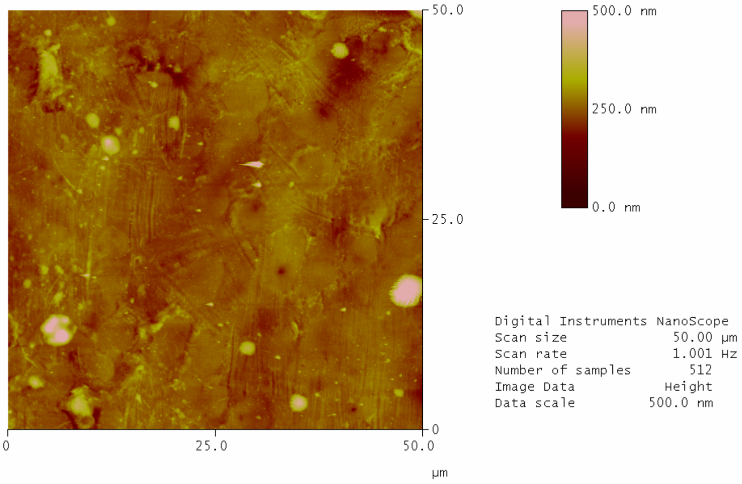
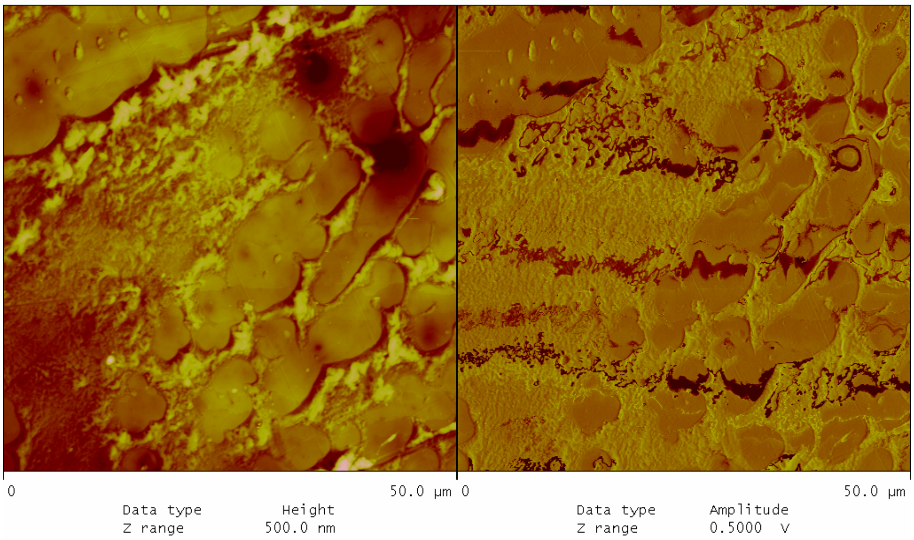


Fig. 3. AFM image of surface of 100 kGy irradiated PCL:PLLA 20:80 containing 5% of untreated coconut fiber.

3.1 FMM – modulated force microscopy

In the FMM mode AFM tip scans sample in contact with the surface applying oscillate force on the cantilever in a way that tip slightly indents the surface testing the elasticity. Tip will deform more the regions with higher elasticity (less rigid) than the rigid regions. Therefore, cantilever deflection will be inversely proportional to the local surface deformation of contact between tip and sample. Then, relative elasticity through sample surface is obtained recording cantilever deflection amplitude in function of scan position on the surface. Regions with higher elasticity appear clearer than rigid regions (Salvadori, 2010).

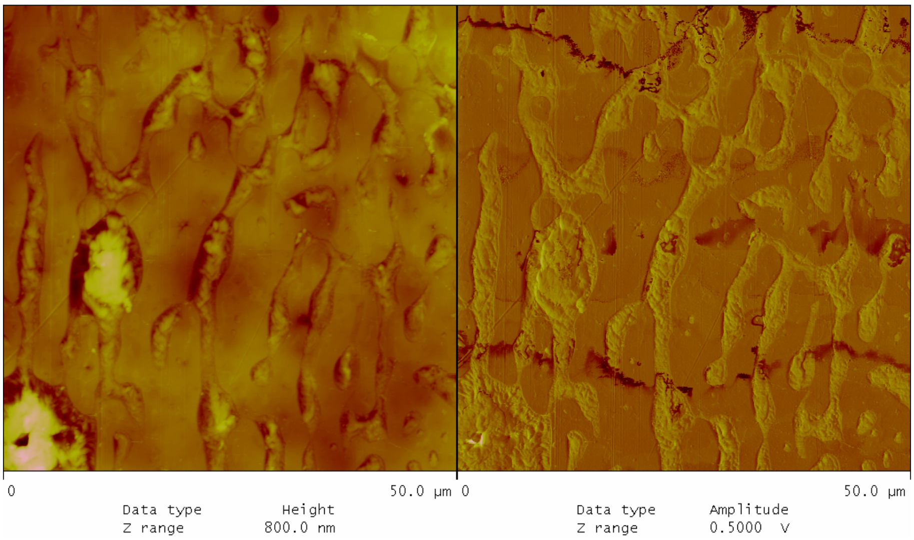
Images of non irradiated composite containing 10% of untreated coconut fiber, obtained by AFM and FMM are shown in Fig. 4 a) and b), respectively; tip holder frequency = 9,10 kHz; (a) z = 500nm; (b) Amplitude = 1.0V; trace mode.



(a) (b)

Fig. 4. Images of surface of non irradiated PCL:PLLA 20:80 containing 10% of untreated coconut fiber: a) AFM, b) FMM

Images of 100 kGy EB irradiated composite containing 10% of fiber obtained by AFM and FMM, are shown in Fig. 5 a) and b), respectively.



(a) (b)

Fig. 5. Images of surface of 100 kGy EB irradiated PCL:PLLA 20:80 containing 10% of untreated coconut fiber: a) AFM, b) FMM

Comparing a) and b) micrographs of Fig. 4 and Fig. 5, it is possible to observe regions that contain different elasticity, in which darker ones observed in FMM images present higher rigidity indicating fiber presence very close to sample surface, affecting elastic properties of sample. Even though fiber had not been observed on the analyzed surface by AFM, FMM technique permitted to observe differences due to fiber presence.

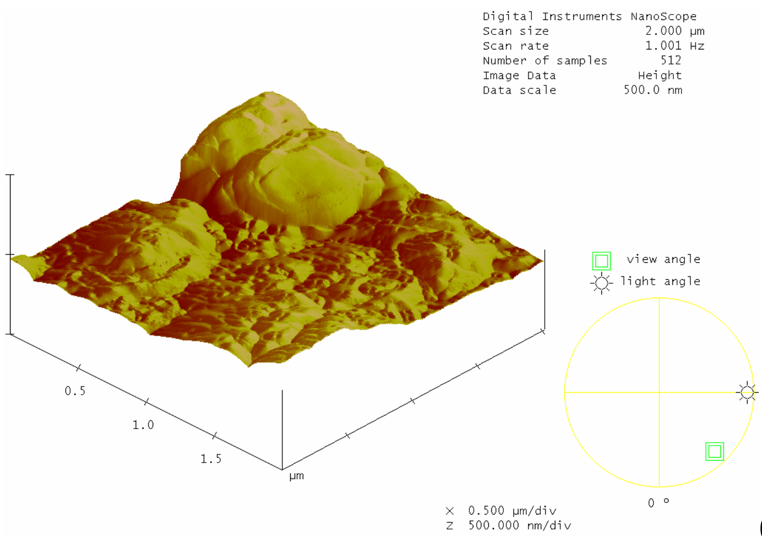
3.2 *AFM tapping mode*

Images of N_{2liq} fractured surface of non irradiated composite containing 10% of untreated fiber are shown in Fig. 6 a), b) and c). It is possible to observe spherical structures on the irregular surface, but it was not possible to visualize fiber presence.

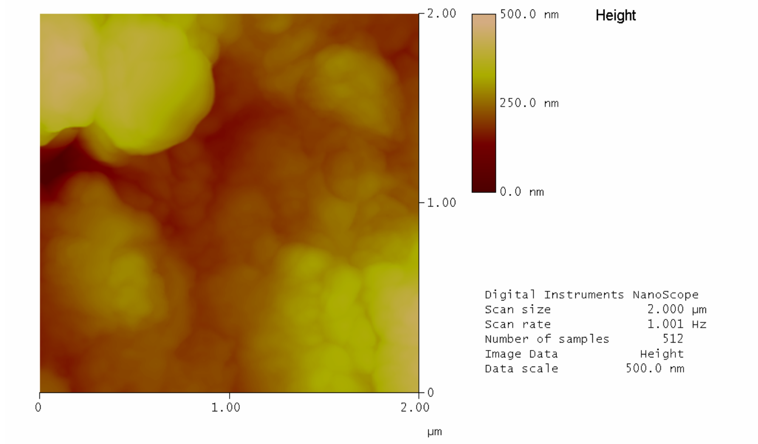
Images of non irradiated composite containing 10% of acetylated fiber are shown in Fig. 7 a) e b). Spherical structures apparently suffered elongation.

Images of 100 kGy irradiated composite containing 10% of untreated fiber, are shown in Fig. 8 a), b) and c). It appears that spherical structures size decreased, probably induced by ionizing radiation.

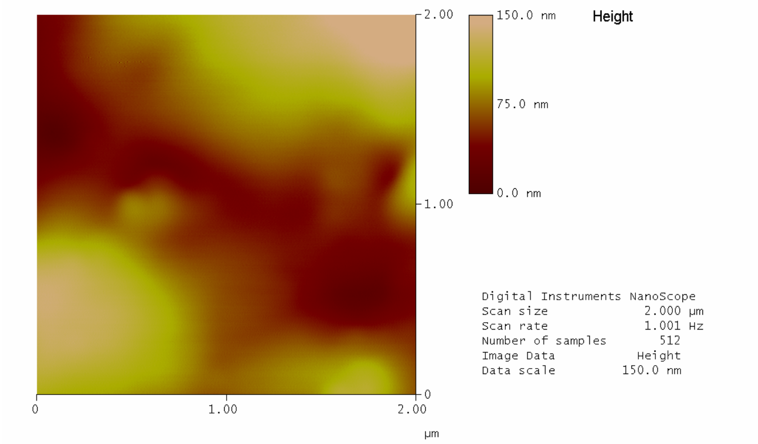
It was not possible to observe the presence of fibers in the studied regions, maybe due to their dispersion on the polymeric matrix. It is important to keep in mind that fibers dimension is hundreds of μm and AFM images hundreds of nm.



(a)

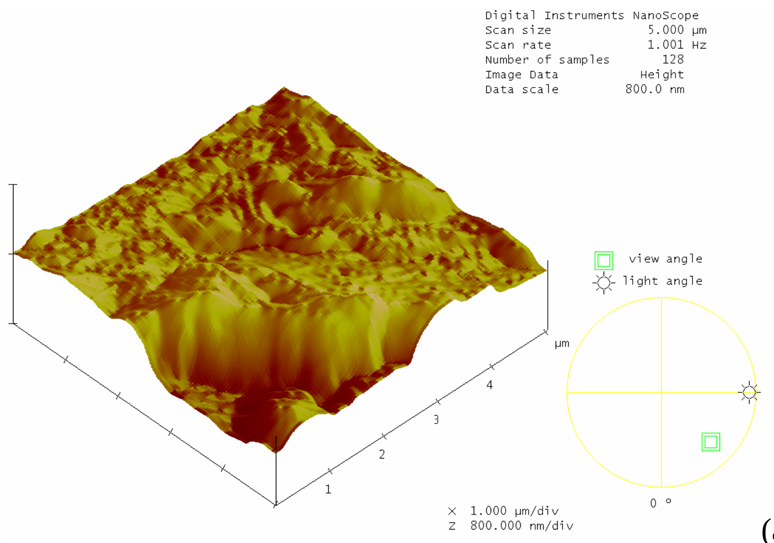


(b)

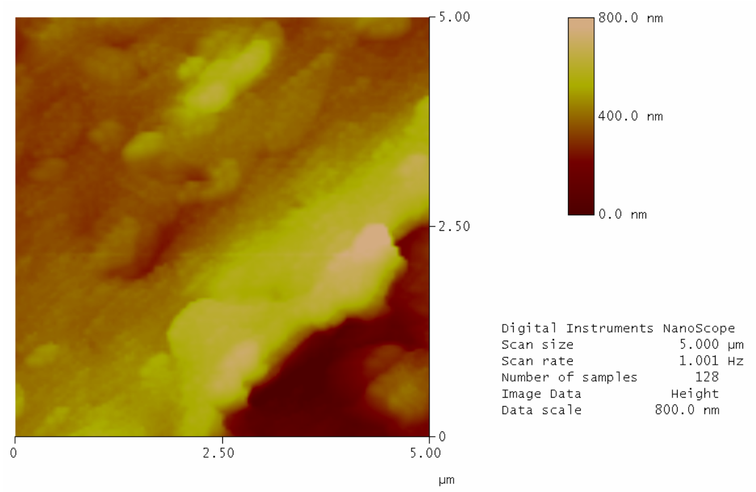


(c)

Fig. 6. AFM image (tapping mode) of N_{2liq} fractured non irradiated PCL:PLLA 20:80 containing 10% of untreated coconut fiber: a) 3D image; b) z=500 nm; c) z=150 nm

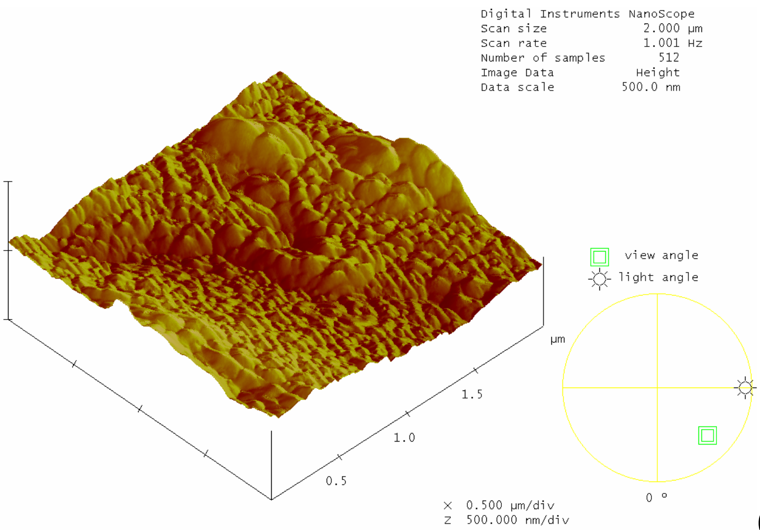


(a)

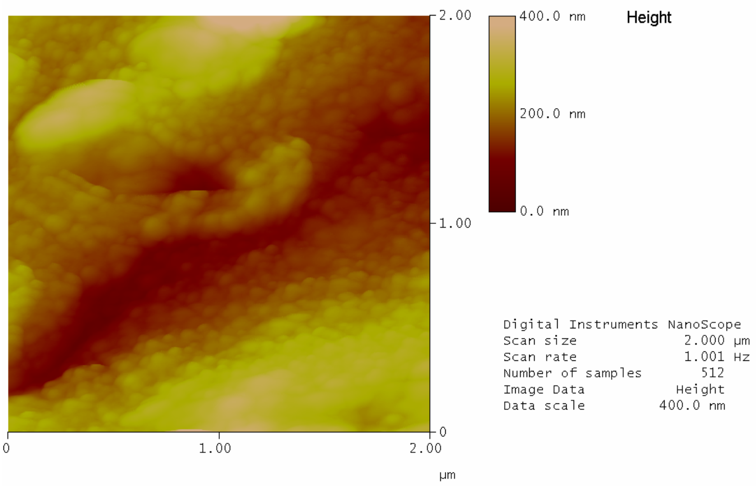


(b)

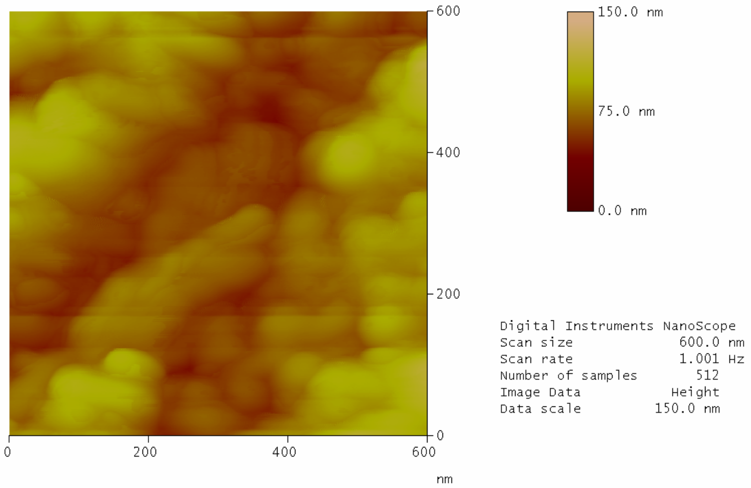
Fig. 7. AFM image tapping mode of N_{2liq} fractured non irradiated PCL:PLLA 20:80 containing 10% of acetylated coconut fiber: a) 3D image; b) scan size 5 µm, z=800 nm



(a)



(b)



(c)

Fig. 8. AFM image (tapping mode) of N_{2liq} fractured 100 kGy irradiated PCL:PLLA 20:80 containing 10% of untreated coconut fiber: a) 3D image; b) z=400 nm; c) scan size = 600 nm, z=150 nm

4 Conclusions

Hot pressed samples surfaces are flat. FMM allowed observing regions with different elasticity, indicating fibers presence near the studied surface. It was possible to observe to observe size decrease of spherical polymeric structures probably due to the absorbed dose.

Acknowledgements

We are grateful to the financial support from IAEA and to the “Laboratório de Filmes Finos do IFUSP” for the SPM facility (FAPESP Proc. 95/5651-0).

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