LLDPE and Natural Fiber Composites Characterization using AFM

Z Zelca[1], S Kukle[2] and J Kajaks[3]

[1, 2] Institute of Design Technologies, Faculty of Material Science and Applied Chemistry, Riga Technical University, Latvia

[3] Department of Polymer Material Technologies, Faculty of Material Science and Applied Chemistry, Riga Technical University, Latvia

E-mail: gusare@inbox.lv

Abstract. The research is focused on the characterization of matrix and filler adhesion, interfacial modifier effects on matrix crystalline formation with filler, depending on the filler modification strategies. Natural fiber filled linear low density polyethylene (LLDPE) composites made from surface modified hemp fiber and waste, zinc oxide, using matrix modifier were prepared by two rolls mill and characterize by Atomic Force Microscope (AFM).

1. Introduction

AFM widely used to investigate the surface topography and surface morphology of materials. On atomically smooth surfaces AFM provides a greater level of detail, profiling of three dimensions, providing measurement of the surface roughness.

AFM is not widely used for natural fiber filled composite characterization because the maximum difference of sample height are often exceeds 60 micrometers and the needle could break. It is difficult to distinguish differences between materials as well, since the method presents the surface topography and fiber particles can be moved with a needle and form vague images.

The most of AFM instruments are conducted at room temperature [1]. The growth of lamellae structure at room temperatures often are impossible because most polymers have phase transitions above room temperature. The several sources reported to use AFM to observe composites at room temperature after heating them for variable times in advance [2].

In situ AFM studies gave the opportunity to observe developing morphologies in a lamellar scale, from the generation of the primary stable nucleus [3] to the development of dominant lamellae, followed by the birth of branching lamellae that splay, leading to the spherulitic morphology [4] with impingement of nearby spherulites [5]. The highest magnification phase images discover lamellar structures embedded in amorphous surrounding. The AFM can be used to investigate a various surface nano treatments.

As main goal of research is focused to characterize the matrix and filler adhesion of natural fibres composite (NCF), matrix crystalline formation with filler, filler dispersion and surface roughness.
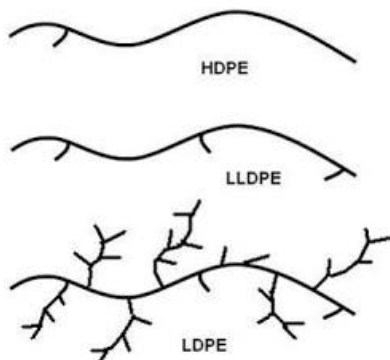
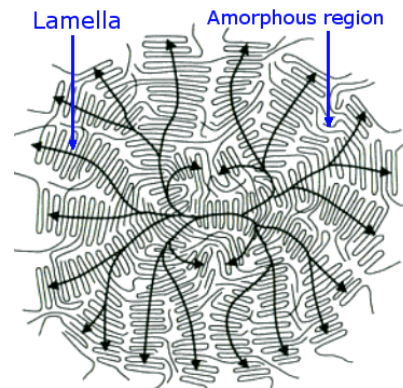**Figure 1.** Schematic model of polyethylene structure [6].

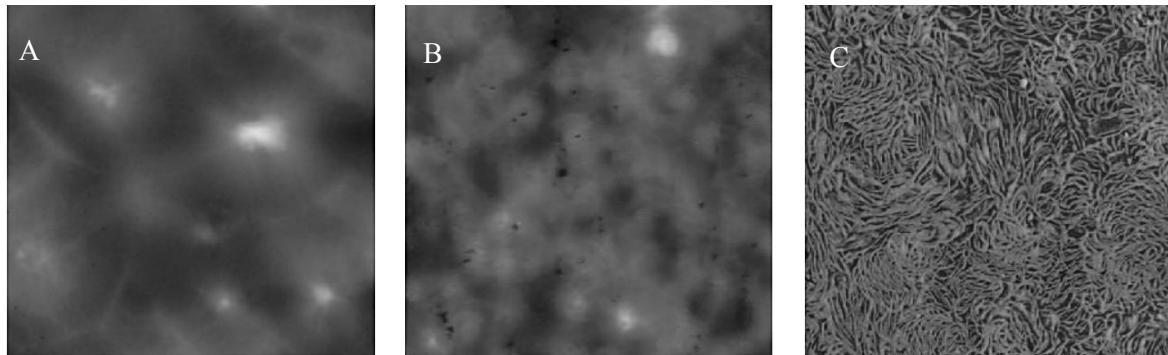**Figure 2.** Schematic image of a spherulite: black arrows indicate direction of molecular alignment [7].

Figure 3. Polymer bundles of lamellae separated by amorphous polymer: A-LDPE, Height Sensor, 18μm x 18μm; B-LLDPE, Height Sensor, 18μm x 18μm; C-LLDPE, Phase Image, 8μm x 8μm [8].

Images analysis of LLDPE and LDPE matrix available in literature shows that it is possible to characterize lamellar order in semicrystalline polymers, in which the amorphous component is in the rubbery state at ambient conditions (Fig. 3). The AFM probe depresses the amorphous inter-lamellar regions and individual lamellae become visible in the images. The linear character of the polymer chains in LLDPE facilitates chain folding and related formation of extended lamellae, which are common for this material with density in the 0.91-0.93 g/cm^3 range [9].
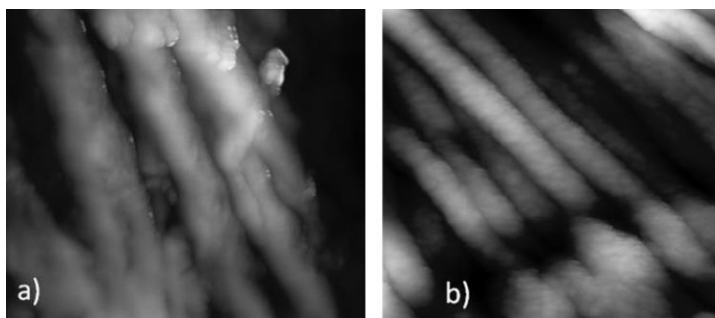

Figure 4. AFM Height images (5×5μm) of hemp fibres after chemical and enzymatic treatments: a) - raw, b) - 10% NaOH [10].

Figure 5. AFM Tapping Phase image of untreated hemp fiber 40x 40μm [11].

This work demonstrated that AFM can be used as a tool to estimate the roughness of modified fibres (Fig. 4 and Fig. 5). AFM is used to the selectively screen treated fibres for composite applications based on the adhesion forces associated with the colloidal interface between the AFM tip

and the fibre surfaces [10]. Height images can shows the different surface roughness of fibers depending on the treatment (Fig. 4), but the images are blurry, without commentary, surface modification type of image can not be ascertained. Fig. 5 shows growth increased relief and damage, but it is not possible to identify the plant sort.

2. Experimental Methods and Materials

LLDPE was used as a polymer matrix of NFC (Tab.1). ZnO nanoparticles (size ~20 nm) are added during the compounding in composite production. Composites were prepared by mixing of components on two rolls mills, granulated and pressed in 0.5 mm thick sheets. Content of hemp fibres or waste (grinded length up to 1 mm) in composites was 40–50 wt% (Tab.2).

For synthesis of silica coating by sol-gel method were used 1.4M tetraethylorthosilicate (TEOS) ($C_8H_{20}O_4Si$) (Alfa Aesar, German), hydrofluoric acid (HF) (SIA"Enola", ES), distilled water and ethanol (C_2H_5OH).

Table 1. Composite matrix properties.

Matrix	Density	Crystalization Point	Peak Melting Temperature	Grade
LLDPE	0.926 g/cm^3	105°C	123°C	LL 6201XR

Table 2. Composite samples.

Sample	Matrix, filler, additives	Filler treatment
1	LLDPE	No filler
1UF	LLDPE, 50 wt% grinded hemp fibers	No treatment
1SF	LLDPE, 50 wt% grinded hemp fibers	Silica coating by sol-gel method
1Z	LLDPE, 2 wt% ZnO nanoparticles	No treatment
1ZUV	LLDPE, 40 wt% grinded hemp waste, 2 wt% ZnO nanoparticles	No treatment

Atomic force microscopy (Bruker Dimension Edge instrument) was used for NFC components interface structure investigation, samples were prepared from melt fractions 140 ^{o}C 10 min on steel disks, sample average weight 0.3 g. Tests were operated in tapping mode using silicone probe (OTESPA-R3), the reference voltage was 2.6+/-0.3V and scan rate 0.2 Hz were applied, micrography sizes 20x20µm till 5x5µm.
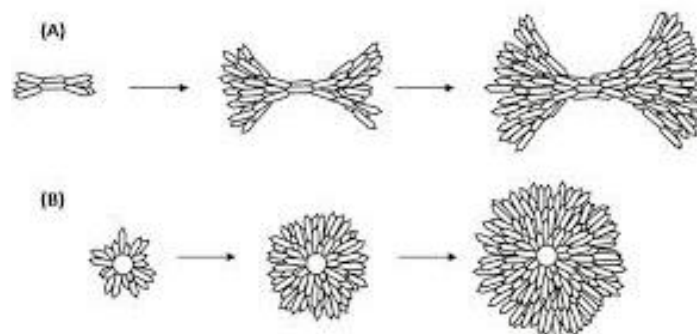
3. Results and Discussion

Figure 6. Lamellaes formation and spherulite formation variants [12].

In order to analyze the composite, it is necessary to obtain images with a matrix and determine changes after additives. The topography images of Fig. 7 shows the structure of LLDPE, Tapping phases can see about 1µm long lamellae formation (Fig. 6, A), but in darker regions - amorphous polymer state.

The LLDPE Tapping Amplitude (Fig. 7 b) topography relief shows spherulite formation directions, Height Sensor indicate sample height 717.7nm (Fig. 7 c). The lighter areas are spherulites formation centers (Fig. 7). The surface topography did not show any significant difference in other sample areas.

The surface roughness of the AFM sample is calculated as a root mean squared (RMS) roughness, it is the geometric standard deviation of the height dimension Z, a specified area referenced to a mean plane. The RMS roughness of the LLDPE (Fig. 7 c) is 81.8 nm, indicating that the surface of the film is smooth.

In comparison with the Phase image of LLDPE (Fig. 3) with a scan size of 8 x 8µm, Phase image lamellaes (Fig.7 a) are not so intertwined that can affect the preparation method of sample or sample density.
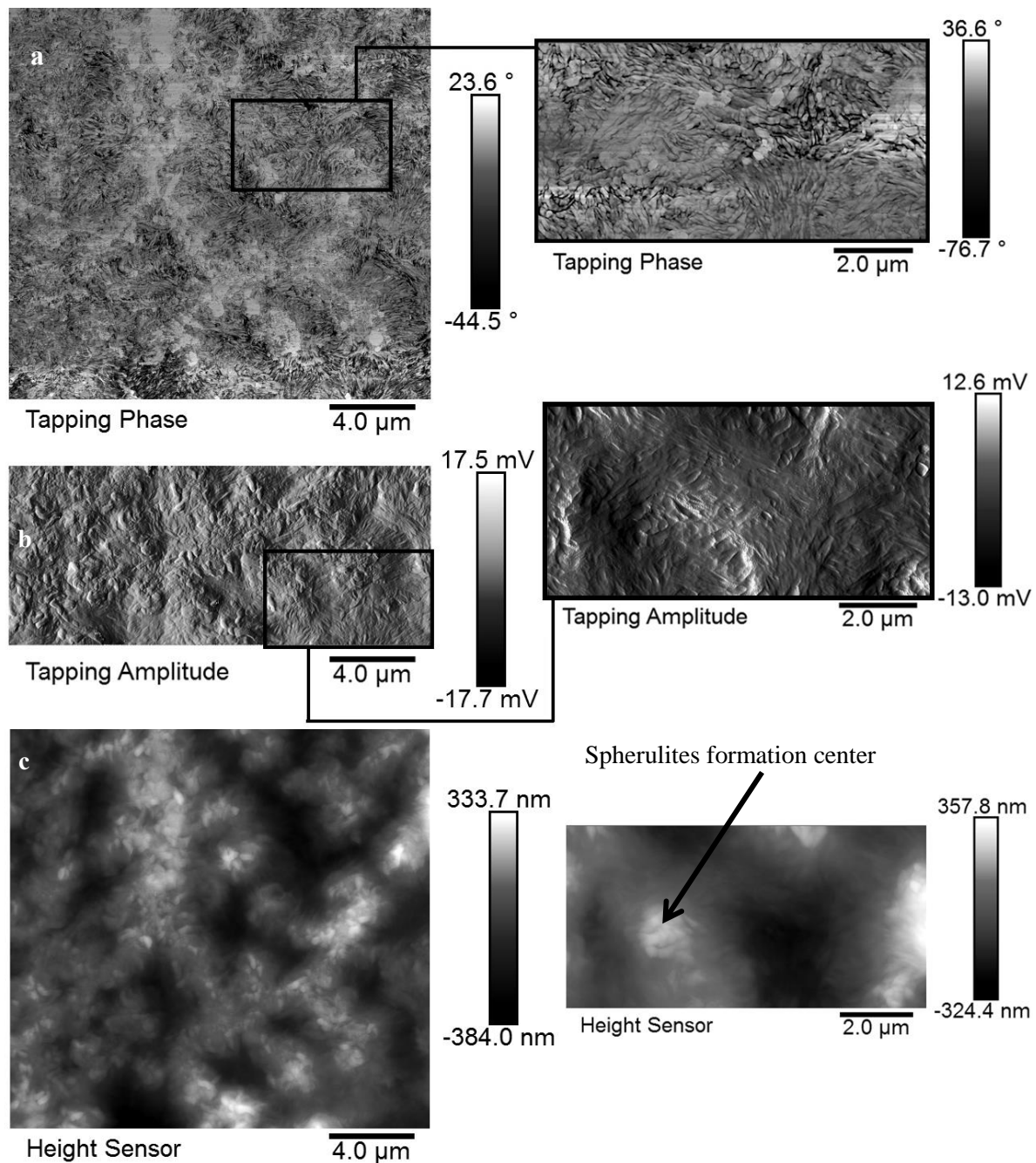

Figure 7. LLDPE micrographs.

Clearly visible boundary between untreated fiber (lighter) and matrix lamellaes (Fig.8, left) could results from the matrix and fiber polar incompatibility. Tapping Phase (Fig. 8, right) show long size lamellaes free formation around the fibers partly seen on the sample surface, amorphous polymer regions (darker) surround fibres.
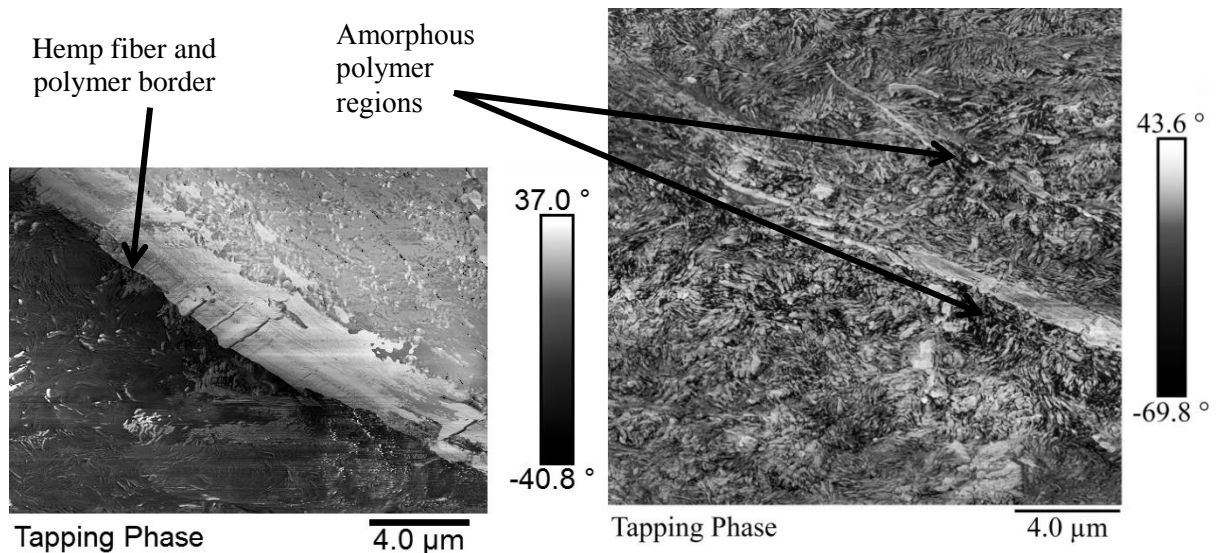

Figure 8. Untreated hemp fiber/LLDPE composite micrograph Tapping Phase (1UF).

Surface height of sample 1SF (Fig. 9) has increased by about 40 nm to compare with the virgin LLDPE (Fig. 7), lamellaes are shorter (Fig. 9, right), spherulite formation direction and height changes could affect fiber additive.
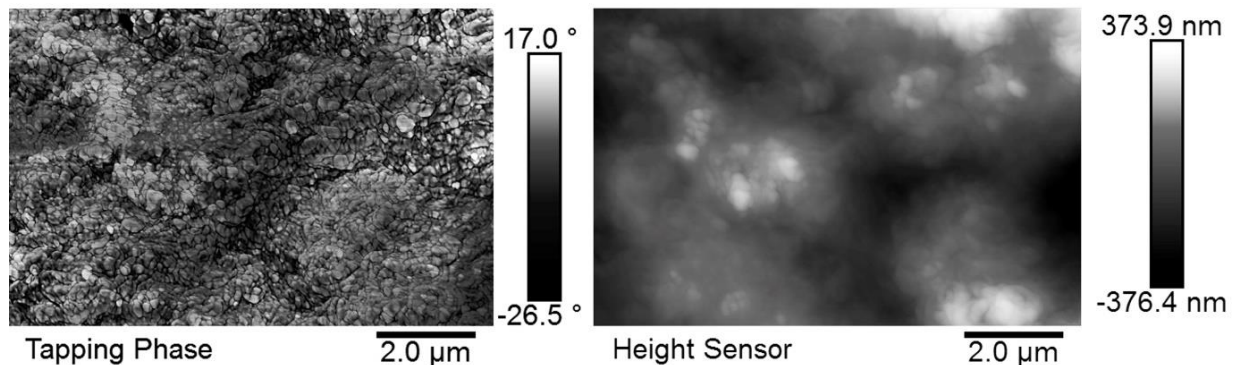

Figure 9. Composite micrograph region without visible fibers (1SF).

Silica coated hemp fiber forming strong links with the matrix (Fig. 10). The hemp surface is smooth, pores and notches are not seen, because they are covered by silane layer or matrix, images allow identified individual fibers and aggregates in different directions scattered into matrix.
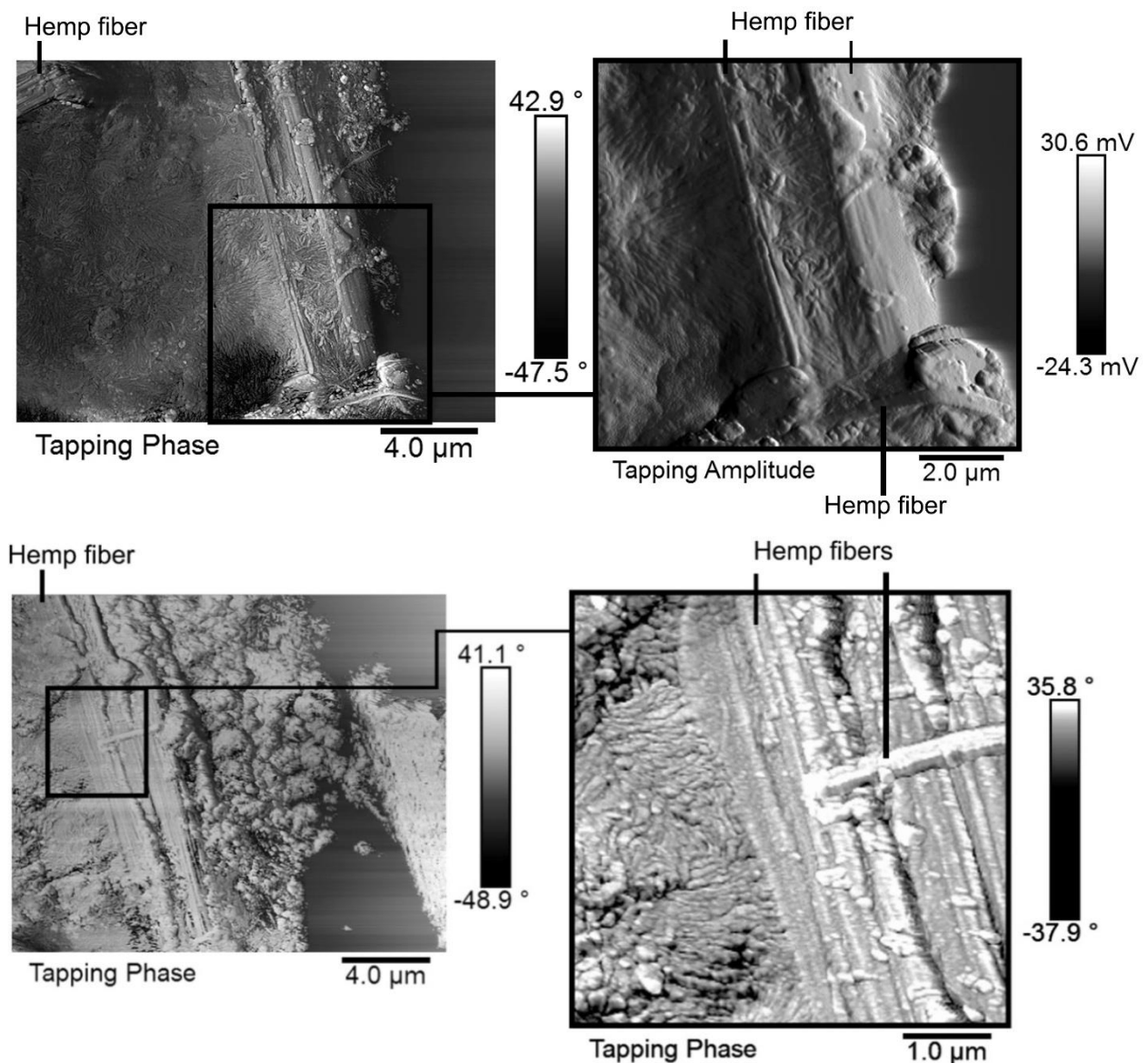
Figure 10. LLDPE/silica sol-gel modified hemp fiber composite micrograph Phase and Amplitude (1SF).

ZnO nanoparticle agglomerates reach up to 1 μm size, lamellaes are difficult to distinguish from ZnO nanoparticles in Phase image (Fig. 11). Height Sensor micrograph surface relief slit shows evenly disperse ZnO in matrix. ZnO agglomerates can reduce composite properties.

The RMS roughness of the sample 1Z (Fig. 11 a) is 487 nm, indicating that the surface of the film is rough in comparison with LLDPE.

In the Fig. 12 (a and c) is difficult to distinguish hemp waste particles due to their irregular shape. The RMS roughness of the Fig. 12 a, c is 508 nm, indicating that the surface of the film is rougher than LLDPE/ZnO nanoparticles composite without waste filler.

ZnO particles interflow with a polymer lamellaes and can not determine the composite components. Two different materials can be distinguished as lighter and darker regions in Phase micrograph (Fig. 12, b). In order to determine the interaction of components requires a higher amount of micrography with an size at least 5x5μm. In comparison with virgin LLDPE composite surface height has increased till about 2 μm.
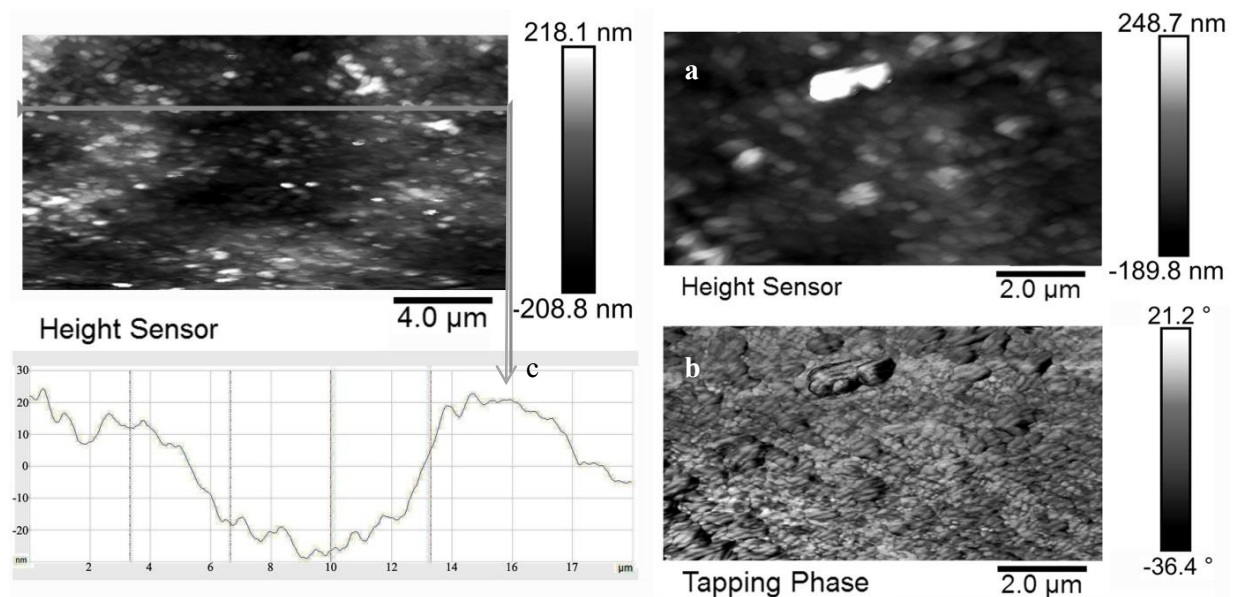
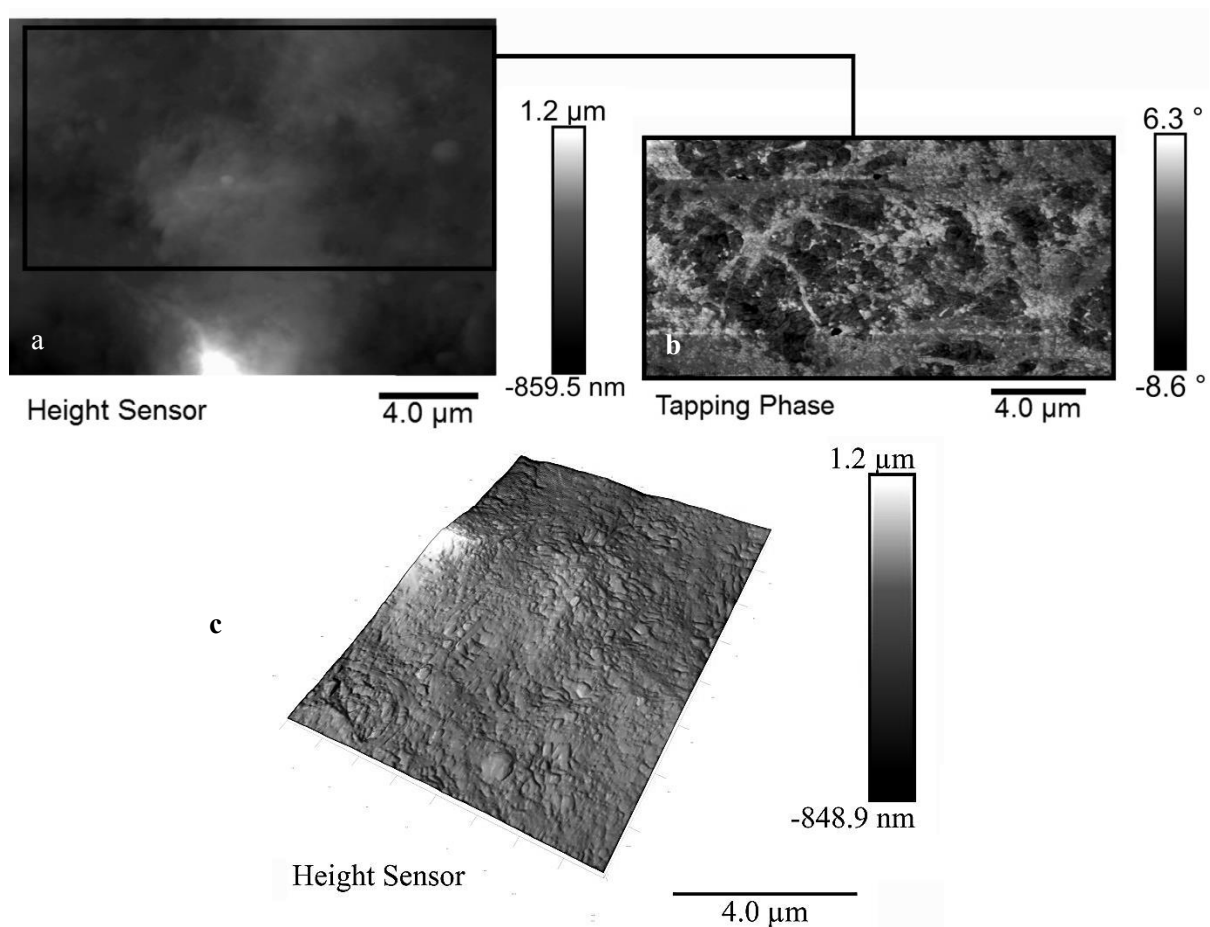**Figure 11.** LLDPE/ZnO nanoparticles composite micrograph Height Sensor (a), Tapping Phase (b) and surface relief slit (c) **(**1Z).

Figure 12. The hemp waste/LLDPE/ZnO nanoparticle composite micrograph Height (a), Phase (b) and 3D Height Sensor (c) (1ZUV).

4.Conclusions

LLDPE samples prepared from melt fraction in AFM micrographs allows to descray spherulite formation and lamellae which helps distinguish matrix of fillers. The obtained micrographs of hemp fiber and matrix boundary surface helps to predict the composite properties. With the sol-gel method treated fibers with lamellae create a stronger link than the untreated fibers. AFM is suitable for studying composite with regular shape fillers.

Zinc oxide nanoparticle additive in composite compounding visible agglomerates about 1 μm size in Hight Sensor but in Tapping Phase lamellaes can not be distinguished from agglomerates. The RMS roughness indicating that the surface of the composite is rough in comparison with LLDPE.

Zinc oxide nanoparticles and grinded hemp waste are difficult to distinguish from the filler matrix into the composite. Micrographs shows that the composite has a different height than the surface of the matrix, but Tapping Phase images can not distinguish between polymer lamellaes and nanoparticles. The hemp waste are irregular in shape, so it is necessary to combine AFM with another methods.

References

[1]   McMaster T J, Hobbs J K, Barham P J and Miles M J 1997 AFM study of in situ real time polymer crystallization and spherulite structure *J. Probe Microsc.* **1** pp 43–56

[2]   Ivanov D A, Jonas A M 1998 Isothermal growth and reorganization upon heating of a single poly(aryl-ether-ether-ketone) (PEEK) spherulite, as imaged by atomic force microscopy *Macromolecules* **31** 4546–50

[3]   Stocker W, Magonov S N, Cantow H J, Wittmann J C and Lotz B 1993 *Macromolecules* **26** 5915

[4]   Pearce R and Vancso G J 1998 Real-time imaging of melting and crystallization in poly(ethylene oxide) by atomic force microscopy *Polymer* **39** pp 1237–1242

[5]   Pearce R and Vancso G J 1998 Observations of crystallization and melting in poly(ethylene oxide)/poly(methyl methacrylate) blends by hot-stage atomic-force microscopy," *J. Polymer Sci.* B **36** pp 2643–2651

[6]   What is LLDPE? (*Electronic Materials*: http://alkatuff.com.au/faq-items/lldpe/)

[7]   Schematic model of a spherulite. (*Electronic Materials:* https://commons.wikimedia.org/ wiki/File:Spherulite2.PNG)

[8]   Jing-jiang Yu and Magonov S N 2007 Application of Atomic Force Microscopy (AFM) in Polymer Materials. Application Note 5989-6926EN

[9]   Magonov S Expanding Atomic Force Microscopy with HybriD Mode Imaging. Application Note 087 NT-MDT Development Inc.

[10] George M Mussone P G Abboud Z and Bressler D C 2014 Characterization of chemically and enzymatically treated hemp fibres using atomic force microscopy and spectroscopy *Appl. Surface Sci.* **314** pp 1019-1025

[11] Zelca Z Kukle S Kajaks J and Kirilovs E 2014 Effect of Fiber Surface Morphology on Water Sorption of Pre-treated Hemp Fiber Reinforced LLDPE Composites *J. Mat. Sci. Textile and Clothing Technology* **9** pp 17-21

[12] Gower L A 2010 Calcium Oxalate and Phosphate Biominerals in Kidney Stones (*Electronic Materials:* http://gower.mse.ufl.edu/research.html)