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THE MECHANICAL PROPERTIES OF BIODEGRADABLE MODIFIED POLYMER PACKAGING: A NANOINDENTATION STUDY

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ABSTRACT

A biodegradable polymer based on polylactic acid (PLA) was chemically modified, and changes in its mechanical material properties were studied using a nanoindentation instrument. During the measurements, the hardness and elastic modulus of the treated samples were determined, and the results were compared to an unmodified control group. Each group consisted of five different samples and t-test was performed to compare the mean difference between the two groups. Statistically significant results were obtained both in the hardness and elastic modulus due to the chemical modification. Both material parameters clearly decreased upon the treatment, and additionally, the structure of the treated samples showed high inhomogeneity. Our results demonstrate that PLA-based packaging has great potential for a wide variety of future applications.

Keywords: Polylactic acid; Nanoindentation; Hardness; Elastic modulus

1. INTRODUCTION

Lactic acid-based biopolymers can be a good alternative to plastics made from petroleum derivatives in food packaging [1]. These polymers can reduce the overuse of non-biodegradable plastics, which has a great importance for the protection of the environment [2]. Polylactic acid has a wide range of uses, for example especially in the medicine as a thin film [3]. The biodegradation of polylactic acid is a great advantage compared to the traditional plastics, but it is important to note that this process occurs in the presence of specific bacteria, so it is essential to provide the right conditions for degradation [4]. Furthermore, the conditions for degradation of the polymer should always be stated to the consumers so they can become aware of it. It is worthwhile to study in more detail both the degradation process itself and the processes that facilitate the degradation. From the point of view of use, it is also very important that the use of lactic acid-based packaging materials is as widespread as possible, since packaging materials are used in very large quantities in everyday life, not only in the food industry, but also in the electronics and textile industries. This rapidly biodegradable biopolymer-based alternative could greatly reduce the environmental impact of plastic packaging made from petroleum derivatives [5].

Nowadays, more and more biodegradable polymer-based packaging materials, e.g., cellulose, have emerged, but they do not have yet the desired stability compared to the traditional petrochemical products which are in daily use [6]. Therefore, our research objective was to investigate the physical and chemical properties of lactic acid-based packaging materials and to study, for example, the effect of different chemical treatments on the structure and degradation of the packaging material. As a first step, the mechanical and elastic properties of treated and untreated lactic acid-based samples was determined using nanoindentation method. The nanoindentation hardness measurement differs fundamentally from the conventional hardness measurement methods. The aim of the nanoindentation is not to determine the size or depth penetration induced by the load during the indentation or to derive a hardness parameter, but rather to determine the whole force-depth penetration curve recorded during loading [7]. This allows for the indirect determination

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of several material parameters such as the modulus of elasticity and hardness of the material. The nanoindentation allows their users to achieve a complex analysis of material behavior, such as the elastic-plastic properties. The measurements showed that the hardness and the elastic modulus of the measured samples are approximately halved as a result of the treatment.

2. MATERIALS AND METHODS

2.1. Materials

For the measurements, pre-made PLA samples derived from food-grade box lid were used which was purchased from Ökosys Ltd.. The PLA samples were modified with carboxylic acid anhydride, the acetic anhydride [$(CH_3CO)_2O$] at room temperature. The PLA is relatively unstable to heat, therefore, a reaction partner that is sufficiently reactive at room temperature was used. To determine the mechanical properties of the final products nanoindentation was performed, which requires a flat and even sample surface. From the lid, 2 by 4 cm pieces were cut out with a thickness of approximately 200 μm. The so-obtained samples were placed in a 20 cm^3 of concentrated acetic anhydride solution. The treatments were carried out simultaneously on five samples at a time and it was repeated three times. The sample treatment duration took 5 days. Acetic anhydride was removed from the samples with 99% ethanol followed by diethyl ether. The samples were then placed in a vacuum dryer at 80 °C for 24 hours. Drying was carried out until the mass of the product became constant. An additional 30 minutes of drying was performed between each mass measurements. For the control measurements, five untreated samples were investigated, and the measurements were repeated three times.

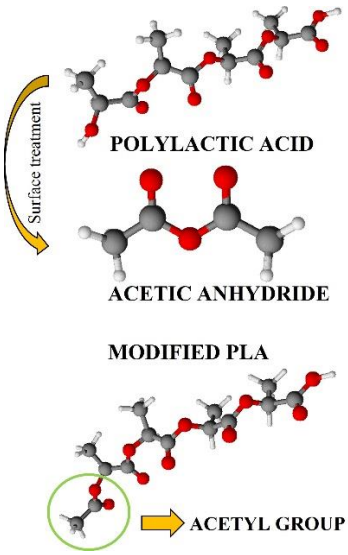

Figure 2 Hypotetical reaction demostrating sample andling

2.2. Nanoindentation

The measurement principle of the nanoindentation is to continuously measure the displacement of the indenter into the material by the progressively applied load [8]. Compared to conventional hardness measurement techniques, it has the advantage of being able to determine the properties of materials as a function of the depth of indentation, leaving an imprint of only a few micrometres in the material, and can be used to test small samples and thin films [9]. From the measured load-displacement curve, the hardness and modulus of elasticity of the sample can be determined. The H hardness can be calculated as the ratio of the P maximum applied load force and the A(h) area of the resulting imprint:

$$H = \frac{P}{A} \tag{1}$$

The area left by the indenter in the material depends on the depth. This A surface area can be expressed if the geometry of the indenter head is known. The three-sided Berkovich indenter tip is used for general purpose investigating the material properties [10]. The E modulus of elasticity is proportional to the dP/dh slope of the recovering curve:

$$E = \frac{\sqrt{\pi}}{2\sqrt{A}} \cdot \frac{dP}{dh} \tag{2}$$

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The maximum loading force changed stepwise during each measurement. The smallest maximum applied loading force was 0.15 mN and the highest 220 mN. This has the advantage of changing the maximum h penetration depth in the material leading to the determination of the surface or bulk phase of the material.

2.2. Statistical analysis

For the statistical evaluation, the material properties, i.e., the hardness and modulus of elasticity values, after a depth of 1.5 µm were used. It was required, since the surface properties influenced drastically the measured values compared to the bulk of the material. Constant material property was observed in both groups after the 1.5-µm layer independently from the depth of indentation. On each sample, 300-600 measurement points were taken on the treated and control groups. On the evaluated hardness and modulus of elasticity the mean values and standard deviations were calculated with a t-test to compare the average differences between the treated and untreated groups. For the statistical analysis IBM SPSS 23.0 (IBM Corp., Somers, NY, USA) software was used. The general α=0.05 significance level was applied for the evaluation.

3. RESULTS AND DISCUSSION

Figure 2 represent a typical force − displacement indentation result for both the treated and control PLA samples.. As shown in Figure 2, the maximum applied loading force was 1 mN and the penetration depth was 0.25 µm and 0.6 µm for untreated and treated samples, respectively. This obtained difference confirms that the physical and mechanical properties of the treated samples changed drastically due to the interaction of PLA with acetic anhydride.

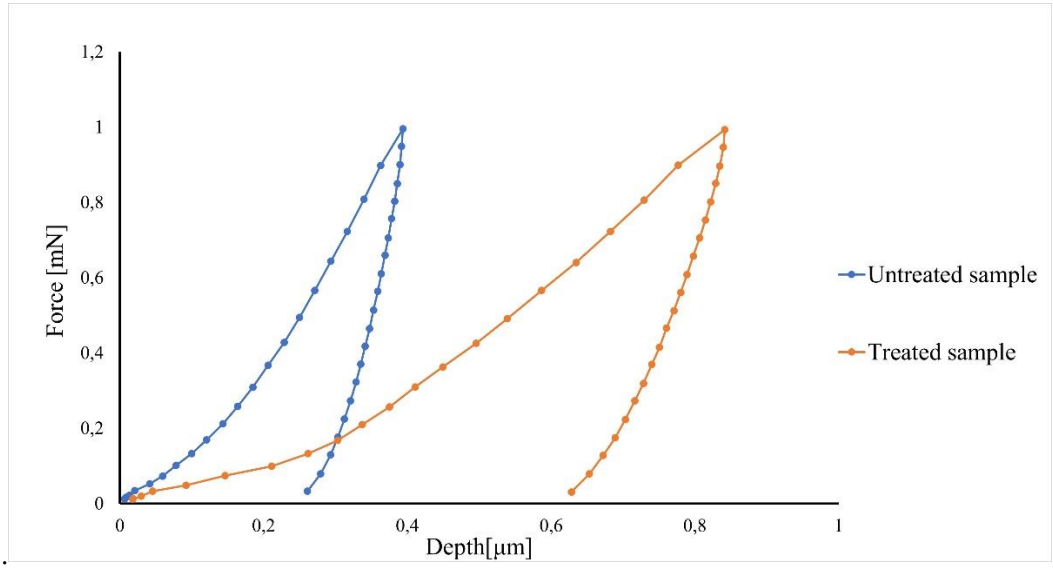

Figure 2. Comparison of representative load-displacement curves for the two groups, e.g., treated versus untreated samples, at a maximal load force of 1 mN.

The calculated hardness values as a function of the depth of indentation are plotted in Figure 3. In both cases the hardness became constant after 1.5 µm depth from the surface. The hardness values of the sample are

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independent from the indentation depth after this depth value. It can be also noted that the hardness decreased to a fraction due to the modification.

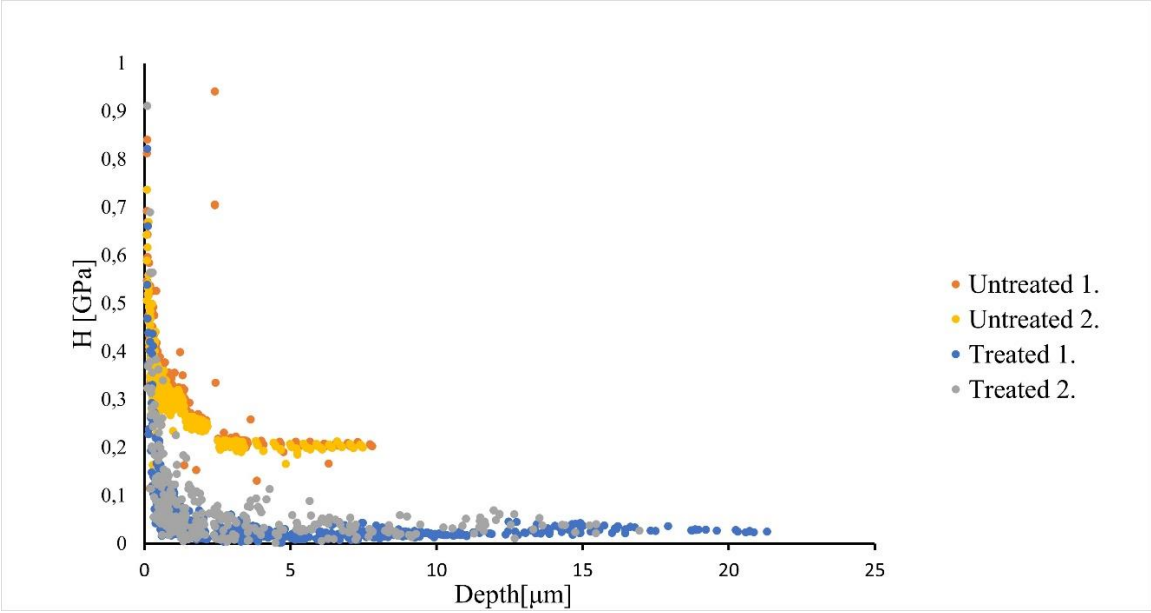

Figure 3. Hardness of the two groups evaluated at different penetration depths.

The modulus of elasticity of the measured samples can be seen in Figure 4. The high modulus of elasticity deviation can be read from the diagram which might be due to the inhomogeneity of the structure of the samples. The modulus of elasticity became constant after a 1.5 um penetration depth as well with a relatively high standard deviation. The modulus of elasticity and stiffness of the untreated samples are 2-3 times higher as the treated sample in average.

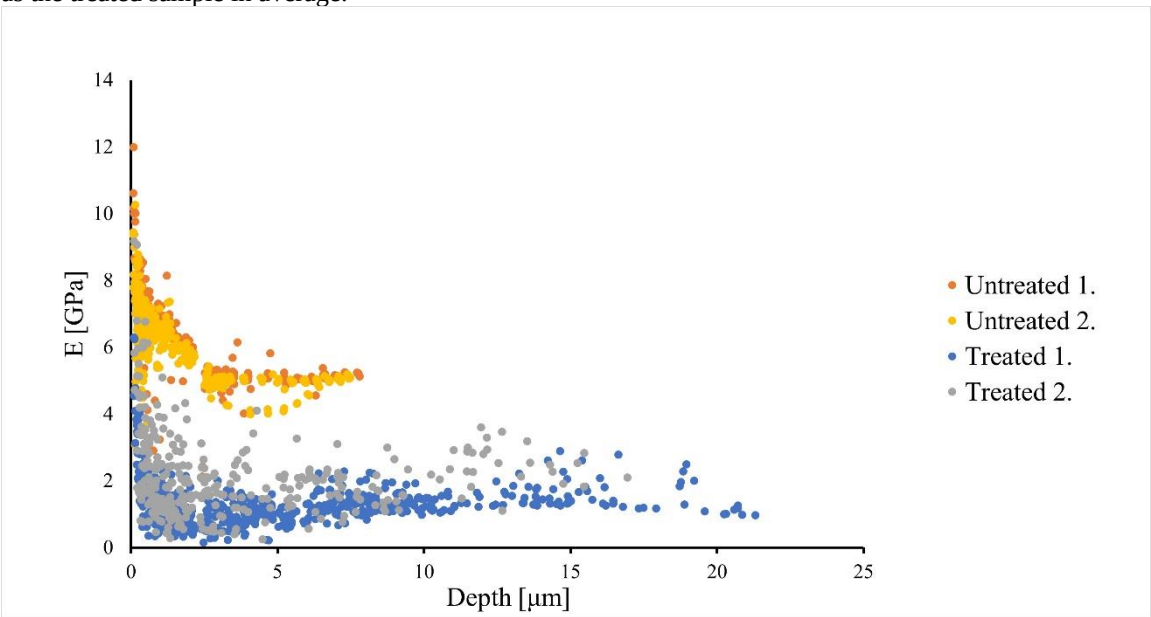

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Figure 4. Indented Young's modulus as a function of depth

The mean hardness and modulus of elasticity values and the corresponding standard deviation of the treated and untreated samples were calculated after 1.5 μm where the measured values became constant, i.e., independent of the depth, see Figure 4. Figure 5 shows the mean modulus of elasticity and hardness with the standard deviation after the 1.5 μm penetration depth. The first untreated sample was compared with the second treated sample. Between the first untreated and second treated sample we found a significant difference ($p<0.001$) between both the average modulus of elasticity and hardness values. The mean value and standard deviations were 5.18±0.68 GPa and 1.85±0.79 GPa in the case of the modulus of elasticity and 0.23±0.08 GPa and 0.04±0.03 GPa in the case of hardness, respectively. Between the second untreated and first treated samples a significant difference was determined as well ($p<0.001$) where the mean modulus of elasticity was 5.1±0.42 GPa and 1.18±0.43 GPa, and the hardness values were 0.21±0.018 GPa and 0.023±0.009 GPa, respectively.

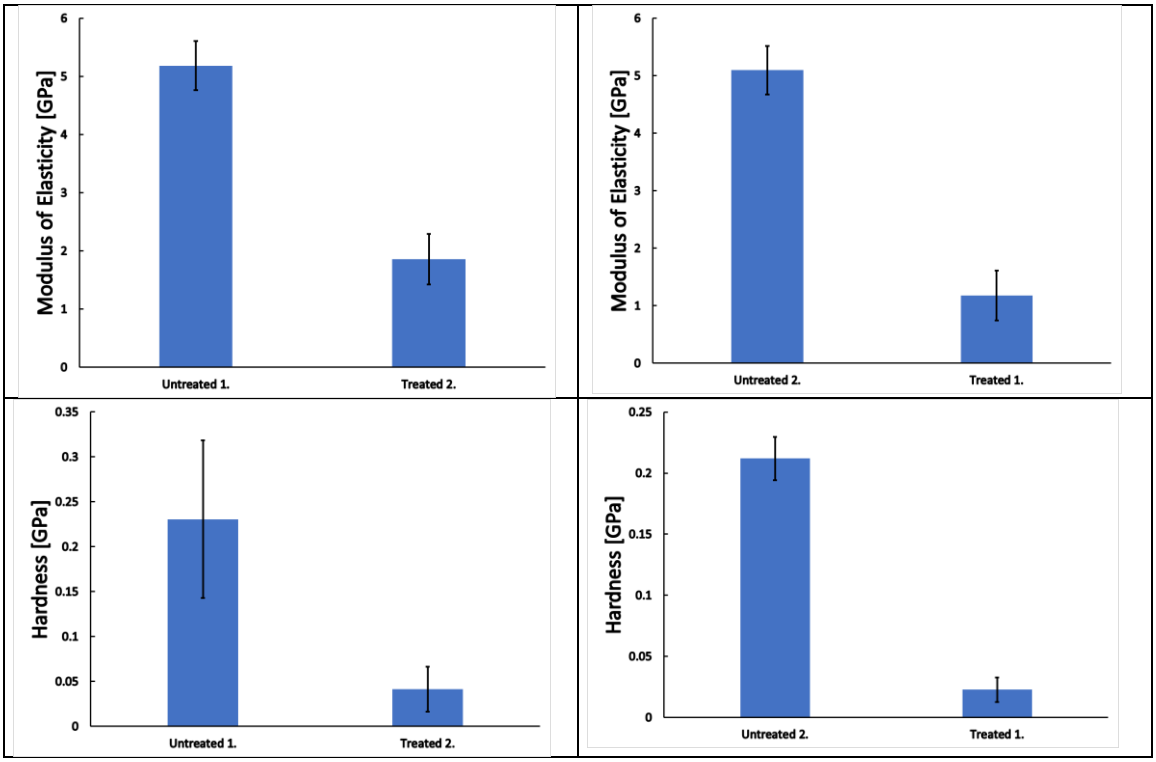

Figure 5. Mean hardness and modulus of elasticity value and standard deviation of the treated and untreated samples.

4. CONCLUSIONS

The nanoindentation results show that the structural change caused by chemical treatment significantly affected the mechanical properties of the PLA. The decrease in both hardness and modulus of elasticity gave the material a more favourable properties in some respects. The stiffness of the modified PLA decreased compared to the untreated and due to that the applicability can be extended to a variety of thin films, foils, coatings. The decrease in hardness can promote processability and handling. The results of this paper may directly contribute to a wider and more diverse use of lactic acid-based packaging materials in the future.

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