

Effect of Abiotic Degradation on the Colorimetric Analysis, Mechanical Properties and Morphology of PLA Composites with Linen Fibers

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ABSTRACT

The manufacturing of composites from biomaterials enables the production of environment- and user-friendly biodegradable products. The matrix of such composite materials is made of biopolymers such as PLA or PGA, while the reinforcement is usually made of natural fibers. Such composites have unique physical and mechanical properties as well as distinctive, eye-catching performance and aesthetic characteristics such as texture, color or roughness. This paper presents the results of colorimetric examination of polymer-linen biocomposite materials under abiotic degradation. The colorimetric examination was made based on a CIELAB model determining the values of lightness, color saturation, chromatic colors and total color difference. The SEM morphology of the specimen surface fracture was also examined. The obtained results show a significant effect of abiotic degradation on the tested parameters.

Keywords: biocomposites, polyactide, flax fiber, thermal degradation, color

INTRODUCTION

Polyactide (PLA) is one of the most important, totally biodegradable polymers. Polylactide (PLA) is a polyester derived from lactic acid that has been the main biodegradable polymer used in biomedical research and applications for the past five decades. As a bioabsorbable polymer, PLA, is one of the most promising biopolymers due to the fact that the monomers may be produced from non-toxic renewable feedstock as well as due to being a naturally occurring organic acid [7, 16]. It is also a leading biomaterial for numerous applications in medicine, as well as in industry, replacing conventional petrochemical-based polymers [16]. It comprises almost 40% of all biodegradable plastics. The period of biodegradability of synthetic polymers such as PE or PS ranges from 500 to 1000 years, while that of PLA ranges between six months and two years [5, 9, 27].

In comparison to other biopolymers, the PLA has numerous advantages, like [7, 17, 21, 23]:

- a) Eco-friendliness – apart from being derived from renewable resources (e.g., corn, wheat, or rice);
- b) Biocompatibility – especially with respect to biomedical applications. A biocompatible material should not produce toxic or carcinogenic effects in local tissues;
- c) Biodegradability – PLA is biodegradable, recyclable, and compostable. The PLA degradation products are non-toxic (at a lower composition) making it a natural choice for biomedical applications;
- d) Processibility – PLA has better thermal processibility compared to other biopolymers such as poly(hydroxyl alkanoate) (PHA), poly(ethylene glycol) (PEG) and poly(γ -caprolactone) (PCL). It can be processed by injection molding, film extrusion, blow molding, thermoforming, fiber

spinning, and film forming;
 e) Energy savings – PLA requires 25–55% less energy to produce than petroleum-based polymers and estimations show that this can be further reduced to less than 10% in the future.

PLA generally come in the form of granulates, and they are processed for the production of films, fibers, plastic containers, and other commodity products [23]. These materials are also used for the 3d printing technique [1, 2, 6].

In order to make it suitable for special applications, PLA is modified by the addition of fillers or preparation of blends [8, 19, 22, 26]. These include starch – to decrease the breakdown time of the polymer and reduce the manufacturing costs, and cellulose fibers – to enhance thermal resistance and rigidity. Modifiers can also be made of inorganic nanofillers such as mica, glass, talc. PLA is often reinforced with synthetic fibers, such as glass and carbon fibers. It can also be reinforced with natural fibers, including wood, cotton, flax, sisal, jute and hemp fibers. A combination of natural fibers and PLA produces an environment-friendly biocomposite material which is one-hundred percent renewable [3, 9, 12].

The use of natural fibers as reinforcement for polymer composites has many advantages due to their properties, such as low density, biodegradability, the ease of recyclability, and acoustic damping. Their use can help decrease thermal expansion of the composite matrix. The processing of such composite materials is constrained by the permissible processing temperature which should not exceed 230°C. If the temperature exceeds 230°C, fibers start to shrink and break down, which has a negative effect on properties of the composite material. If fibers are subjected to heating, this may cause the physical and/or chemical changes in their structure, such as depolymerization, hydrolysis, oxidation, dehydration, decarboxylation and recrystallization. In order to prevent these defects, it is necessary to restrain/reduce the temperature range and the processing time [12, 14, 24].

Linen fiber is made up of bundles containing 10–40 individual fibers with a length of approx. 30 mm and a diameter of 0.2 mm. These single fibers are bound together and elongated by pectin, forming a 60–90 cm long bundle. Linen fiber is composed of 65–70% cellulose, 3–5% lignin, approx. 15% hemicellulose and 5–7% pectin (and up to 5% phenol, ash, wax). Linen fibers have

very high vibration damping properties – their vibration damping ability is two and a half times higher than that of carbon fibers. Long linen fibers have lower tensile properties than short fibers [15, 18, 20, 25].

The shortcomings of natural fibers include their hydrophilic nature, low thermal resistance and a high scatter of mechanical properties. Studies are conducted to develop the solutions for enhancing the fiber strength e.g. by softening or boiling. It is also vital to identify the mechanisms affecting the phase boundaries in polymer-matrix fibrous composites. The adhesion between hydrophilic natural fibers and hydrophobic polymer matrix is very low. Most natural fibers are characterized by porosity, which leads to increased humidity absorption by the fibers and reduced adhesion [12].

In terms of the use of natural materials for consumer products, the key properties are the strength, processability, shape and size stability along with thermal and material stability of these materials. The examination of abiotic degradation of PLA constitutes a method for determining the stability of composite materials [4, 10]. One of the effects of biomaterial degradation is the change of color components such as the lightness – luminance of a color (L^*), base color (a^* , b^*), total color difference (ΔE) and saturation (C^*). Color measurement allows a qualitative analysis of different material types. Color determination can be performed based on the CIELAB color space model, enabling the expression of color via Cartesian and cylindrical coordinates. According to this model, the L value (ranging from 0 – the darkest black to 100 – the brightest white) is expressed with Cartesian coordinates as [11]:

$$L = 116 * f\left(\frac{Y}{Y_0}\right) - 16 \quad (1)$$

while a^* and b^* :

$$a = 500 \left(f\left(\frac{X}{X_0}\right) - f\left(\frac{Y}{Y_0}\right) \right)$$

$$b = 200 \left(f\left(\frac{Y}{Y_0}\right) - f\left(\frac{Z}{Z_0}\right) \right)$$

where: X, Y, Z denote the trichromatic color components obtained by the transformation of the components

R – red,
 G – green,

B – blue, while X_o , Y_o , Z_o are the component of white light used as a reference color.

For the equations above, the function $f(t)$ is defined with [11]:

$$f(t) = \begin{cases} \sqrt[3]{t}, & t > 0,008856 \\ \frac{903,3t + 16}{116}, & t \leq 0,008856 \end{cases} \quad (2)$$

where the functions f_x , f_y , f_z are expressed as:

$$\begin{aligned} f_x &= \frac{a}{500} + f_y \\ f_z &= f_y - \frac{b}{200} \\ f(y) &\begin{cases} \frac{L + 16}{116}, & y_o > 0,008856 \\ \frac{903,3y_o + 16}{116}, & y_o \leq 0,008856 \end{cases} \quad (3) \end{aligned}$$

In the CIELAB model, the saturation C and the total color difference ΔE are respectively expressed as [11]:

$$c = 13L\sqrt{(a - a_o)^2 + (b - b_o)^2}$$

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2}$$

The condition of objects made from a given material essentially depends on their physical properties, primarily their mechanical strength and color. For this reason, the decrease in total color difference of the specimens induced by ageing is one of the basic parameters describing the life of a given material under specified storage or exposure conditions. For many polymeric materials and low molecular compounds, the changes in molecular structure caused by the impact of various destructive factors (e.g. heat, UV radiation) are reflected in the change of their color [24].

The objective of this study was to investigate whether the colorimetric, mechanical properties and morphology examination can be used for assessing the degree of degradation of polymeric biomaterials.

MATERIALS AND METHODS

The study was performed on a linen fiber-reinforced composite material with polyactide matrix, produced by injection molding. The composite material was subjected to thermal degradation

to investigate its effect on the color and morphology of the composite.

The matrix was made of granulated polyactide, PURAPOL L130. Compared to the standard PLA, it has a higher melting temperature and a higher crystallization rate. Selected properties of this polyactide, as specified by the manufacturer, are listed in Table 1.

The reinforcement was made from long, combed organic linen fibers. In order to obtain short fibers, the long fibers were cut with a cutter to the length ranging from 5 to 10 mm.

Dumbbells (Figure 1) were produced by injection molding with the ARBURG Allrounder 320C plastic injection molder. The injection molding process was described by the following parameters: the temperatures of individual zones of the plasticizing unit were set equal to 40°C, 150°C, 180°C, 200°C, 200°C and 200°C, respectively; the injection pressure was set equal to 90 MPa; the clamp pressure was set equal to 90 MPa; the cycle time was set equal to 43.57s;

Table 1. Selected properties of PURAPOL L130, according to the product data provided by the manufacturer

Property, unit	Value
Density, kg/m ³	1240
Stereochemical purity, % L-isomer	min. 99
Melt flow index, g/10min	16
Melting temperature, T _m , °C	175
Glass transition temperature T _g , °C	55 ÷ 60
Tensile modulus, MPa	3500
Tensile strength, MPa	50
Elongation at break, %	max. 5



Figure 1. Dumbbell specimens with 0%, 1%, 2%, 3%, 4% and 5% linen fiber contents

the injection time was set equal to 3s, and the cooling time was set equal to 30 s. As a result of injection molding, moldings were produced with the following linen contents: 0%, 1%, 2%, 3%, 4% and 5%. During the process, the moldings in the shape of specimens for mechanical testing were obtained. The amount of specimens was 100 pieces, each. Five samples were tested in one test each time, both before and after degradation. The results presented are based on the mean values of five measurements, in accordance with the current subject standards.

The specimens were subjected to thermal degradation for 4 weeks at 60°C, in compliance with ASTM F1980 – 07:2011. The process parameters were applied in such a way so as to replicate a 12-month degradation at normal temperature. The degradation process was carried out in the SLW 115 TOP + drying oven with the temperature range of 0 ÷ 300°C.

The morphology of surface fracture of the specimens after tensile testing was examined with the PHENOM tabletop scanning electron microscope.

The examination of colorimetric analysis of the composite material was conducted with the X-rite Ci4200 benchtop sphere spectrophotometer connected to a desktop computer provided with the Color iControl Ink software. The assessment of color was performed with the use of the CIELAB color space which enables the description of color in Cartesian coordinates. It is based on the following color components: L* (the lightness component), a* and b* (a* – the green-red component, b* – the blue-yellow component) and C* (saturation).

The mechanical properties test was conducted with tensile machine Zwick Z010 in compliance with ISO 527:2012.

RESULTS

Colorimetry

The examination of color of the polymer-linen composite materials led to obtaining photometric images and spectra profiles, as shown in Figures 2 and 3. The results of the measurement



Figure 2. Photometric images of the specimens: a) before degradation b) after degradation

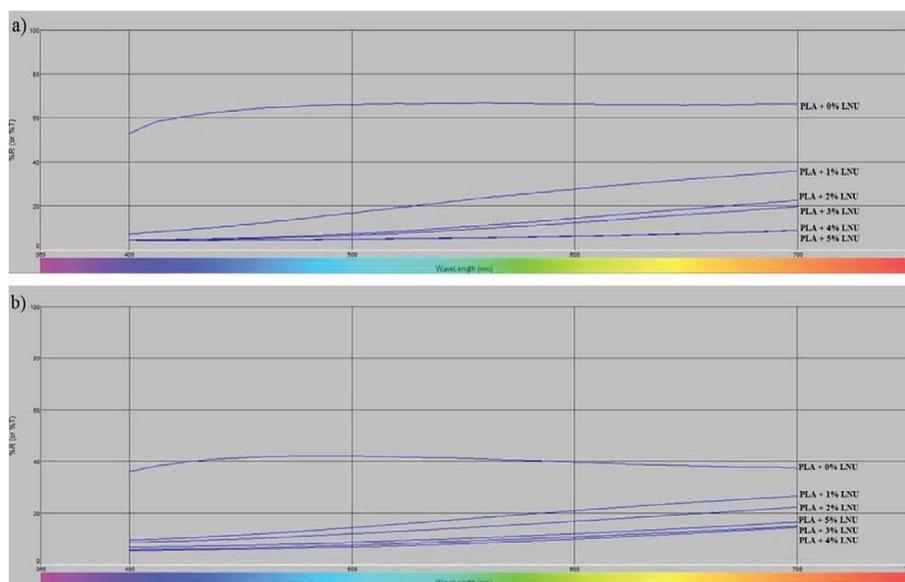


Figure 3. Spectral profiles of the specimens: a) before degradation b) after degradation

of the CIELAB color space components for the specimens before and after degradation are shown in Figures 4–10.

As a result of degradation, the absorption spectra of the specimens with 0%, 1%, 2% and 3% linen fiber contents decrease proportionally to increasing the linen fiber content. On the other hand, the specimens with 4% and 5% linen fiber contents have slightly higher absorption spectra.

The plot illustrating the relationship between the total color difference and the linen fiber content in the specimens before and after degradation (Figure 4) shows that degradation causes the change in color. The greatest change in color resulting from degradation can be observed for the specimens with no linen fiber content, while the smallest for the specimens with 3% linen fiber content.

The plot of lightness values and linen fiber content of the specimens before and after degradation (Figure 5) shows that, as a result of degradation, the specimens with 0%, 1%, 2% and 3% linen fiber contents become darker, while the specimens with 4% and 5% linen fiber contents become lighter. The specimens with 0%, 4% and

5% linen fiber contents show significant changes in the lightness value. As a result of degradation, the lightness value of the specimens with no linen fiber content decreases by 18.35%, whereas in the case of the specimens with 4% and 5% linen fiber contents, their lightness value increases by 28.66% and 25.24%, respectively. The specimens with 1%, 2% and 3% linen fiber contents show slight changes in the lightness value due to degradation, amounting to less than 6%.

In the plot illustrating the relationship between the value a^* and the linen fiber content in the specimens before and after degradation (Figure 6), one can observe that due to the addition of linen fiber, the color of the specimens changes from green to red. As a result of degradation, the value a^* decreases for the specimens with 0%, 1%, 2% and 3% linen fiber contents, which means that they become less red; on the other hand, its value increases for the specimens with 4% and 5% linen fiber contents, which means that they become redder.

The plot illustrating the relationship between the value b^* and the linen fiber content in the specimens before and after degradation (Figure 7) shows

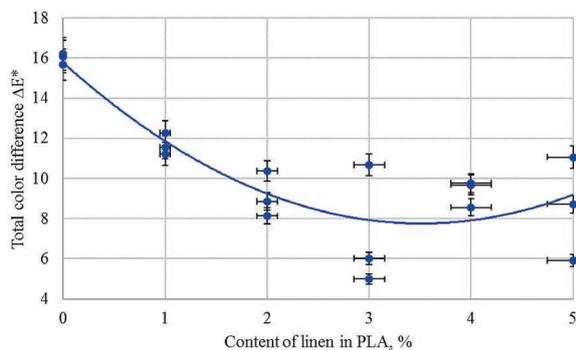


Figure 4. Total color difference versus linen fiber content of the specimens before and after degradation

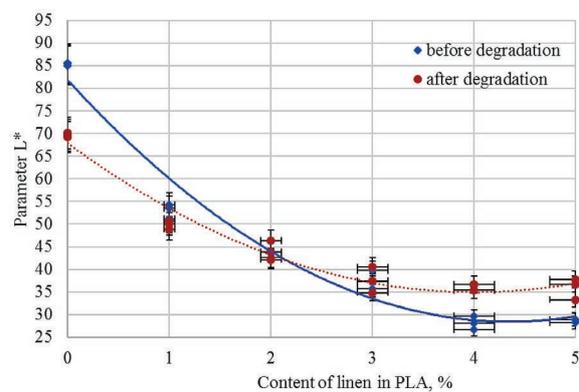


Figure 5. Value L versus the linen fiber content in the specimens before and after degradation

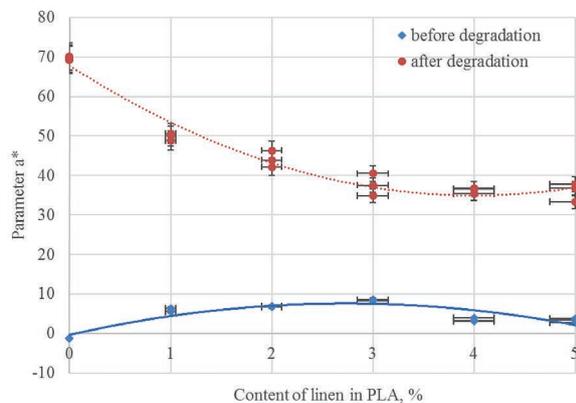


Figure 6. Value a^* versus the linen fiber content in the specimens before and after degradation

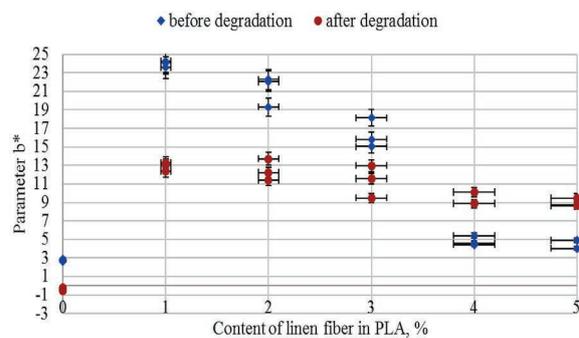


Figure 7. Value b^* versus the linen fiber content in the specimens before and after degradation

that the addition of linen fibers leads to an increase in the value b^* , which means that the specimens become yellower. As a result of degradation, this parameter decreases for all tested specimens, except for those with 4% and 5% linen fiber contents. With decreasing this value, the specimens become less yellow but with its increase the color of the specimens becomes yellower.

The diagram showing the relationship between color saturation and the linen fiber content of the specimens before and after degradation (Figure 8) reveals that the highest color saturation is obtained for the specimens with 1%, 2% and 3% linen fiber contents. As a result of degradation, the color saturation decreases by approx. 48% for the specimens with 1% linen fiber content, by 34% for the specimens with 2% linen fiber content, and by 32% for the specimens with 3% linen fiber content. The color saturation of the specimens with 4% and 5% content of linen fiber is lower prior to degradation than after degradation. Due to degradation, the color saturation of these specimens increases by nearly 37%. The pure polyactide specimen exhibits very low color saturation, the value of which slightly decreases after degradation.

The plots illustrating the relationships between the values a^* and b^* and the linen fiber content

in the specimens (Figures 9 and 10) also demonstrate that prior to degradation, the differences in these values for individual specimens are higher than those observed after degradation when these differences become insignificant. It can therefore be claimed that degradation decreases the differences in color of individual specimens.

Mechanical properties

The mechanical test was conducted for the samples before and after degradation process. The results of mechanical properties was shown in Table 2. The results shown that abiotic degradation in the assumed degradation parameters, has a slight impact on the measured properties.

For the samples before degradation, the Young’s modulus increases by 10% with the increase of content of linen fibers from 0% to 5%, while tensile strength and elongation decrease by 19% and 27%, respectively. For the samples after degradation, the change of the linen fibers content from 0% to 5% caused Young’s modulus decrease by 4% and tensile strength increase by 23% and elongation decrease by 32%.

Abiotic degradation process also caused changes of the measured mechanical parameters in the tested samples. The changes are visible

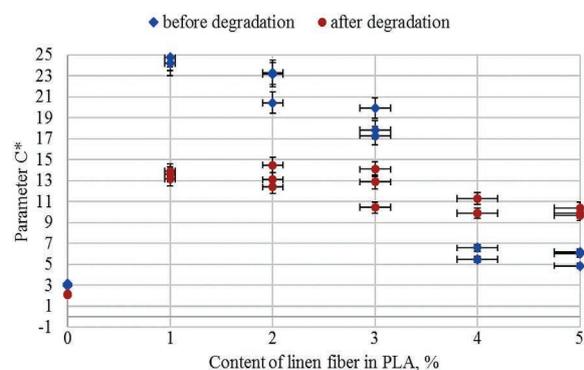


Figure 8. Color saturation versus linen fiber content in the specimens before and after degradation

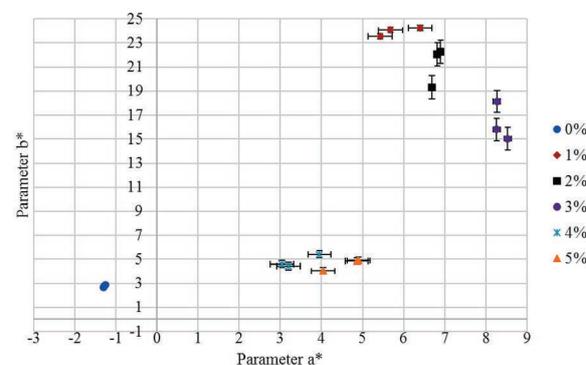


Figure 9. Color saturation versus linen fiber content in the specimens prior to degradation

Table 2. Results of mechanical properties for the samples before and after degradation

Materials	Results for samples before degradation			Results for samples after degradation		
	E_t , MPa	σ_m , MPa	ϵ_m , %	E_t , MPa	σ_m , MPa	ϵ_m , %
PLA + 0% linen fibers	2568.00	66.19	3.51	2537.21	71.63	3.56
PLA + 1% linen fibers	2575.94	62.73	3.34	2619.35	68.18	3.39
PLA + 2% linen fibers	2642.39	62.82	3.31	2618.53	66.41	3.28
PLA + 3% linen fibers	2708.80	61.12	3.22	2651.33	61.75	2.98
PLA + 4% linen fibers	2722.89	54.03	2.74	2603.39	53.41	2.42
PLA + 5% linen fibers	2836.75	53.42	2.53	2642.60	54.71	2.42

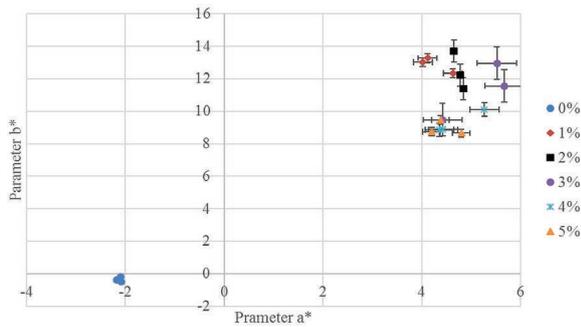


Figure 10. Color saturation versus linen fiber content after degradation

especially for the measures of Young's modulus and elongation in samples with 3% and greater linen fibers content. The average value these changes is 5% for Young's modulus and 7% for elongation. For lower contents of linen fibers (from 0 to 2%) the tensile strength value slightly increases due to degradation. Above 3% of linen fibers, these values are close to the results before degradation. This may be due to the reinforcing effect of the fibers themselves that have not yet degraded, which is related to the supermolecular structure of the moldings obtained. At lower enhancement contents, the fibers were distributed homogeneously and were only in the core of the sample. With higher contents of linen fibers, agglomerations of fibers located in the outer layer of the sample were visible. As a result of the temperature, PLA was degraded, and the linen fibers were partially stripped of the warp, which was visible in the sample with a higher fiber content.

Morphology SEM

Figures 11–16 compare the morphology of surface fracture caused by tensile testing in the specimens before and after degradation.

The morphology examination reveals that the specimens undergo brittle fracture. The SEM image of the fracture surface of the solid specimen that was not subjected to degradation shows the presence of more extensive and more jagged fragments caused by the specimen rupture. The SEM image of the surface fracture of the specimen after degradation is free from such fragments (Figure 11).

In addition to that, one can observe a separation of the fiber surface from the matrix (Figures 12 and 13), which indicates weak adhesion between the fibers and the polymer matrix. The fiber surface damage of the specimens after degradation is more visible than that of the specimens prior to

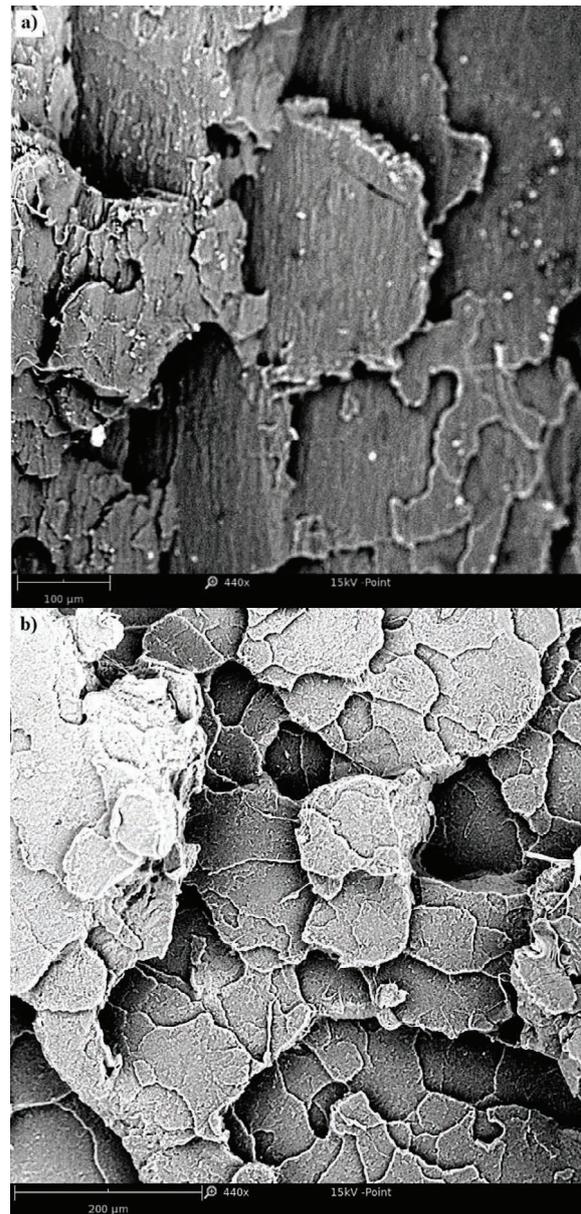


Figure 11. Morphology of the specimen with 0% linen fiber content: a) before degradation b) after degradation

degradation. One can also observe that the presence of linen fiber prevents crack propagation.

The nature of fiber rupture is shown in Figures 14 and 15. The specimens subjected to ageing show a more damaged surface of the fibers. In the SEM images of the specimens that were not subjected to ageing, one can see visible empty spaces resulting from the slippage of individual fibers.

Figure 16 reveals a considerable volume fraction of the fibers. One can observe the holes created due to the slippage of individual fibers, which points to weak fiber-matrix adhesion. One can clearly see the change in the matrix structure due to degradation.

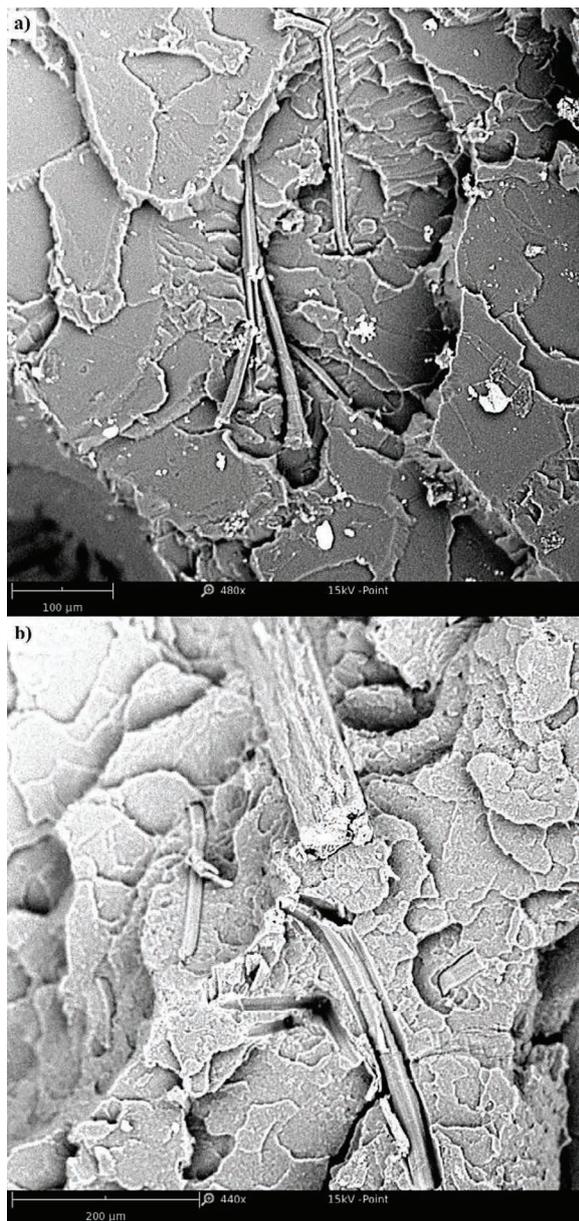


Figure 12. Morphology of the specimen with 1% linen fiber content: a) before degradation b) after degradation

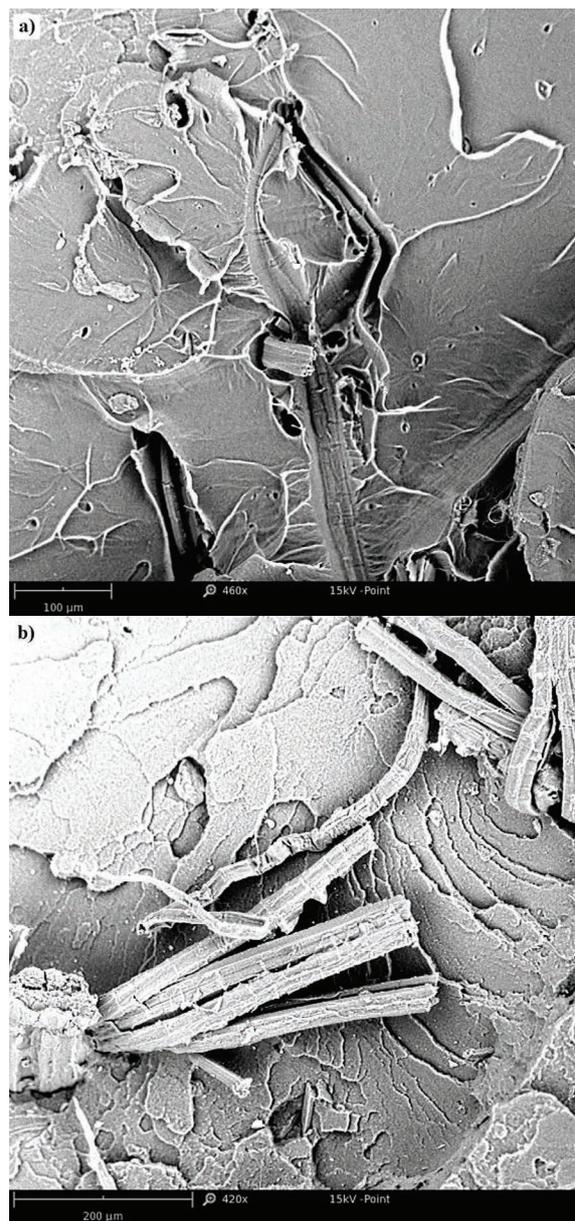


Figure 13. Morphology of the specimen with 2% linen fiber content: a) before degradation b) after degradation

CONCLUSIONS

Polymers are widely used in the industry, which poses a problem regarding their waste management. The objectives of this study was to recognition about the characteristics of a fully biodegradable composite and to investigate whether the use of natural materials as composite reinforcement can accelerate the process of their degradation.

The structural analysis has revealed significant changes of the composite morphology due to the increase in the linen fiber content and

degradation. The microscopic image analysis showed fiber agglomeration for the samples containing 3–5% linen fibers. As a result of degradation, the fibers were torn and fragmented, and the agglomeration areas decreased.

The spectrometric analysis results have demonstrated a significant change in color of the test specimens. The observed changes in the color and morphology of the polyactide-matrix composite reinforced with linen fiber indicate the onset of degradation processes, which is reflected in the changes in the composite structure and the start of decomposition of the material.

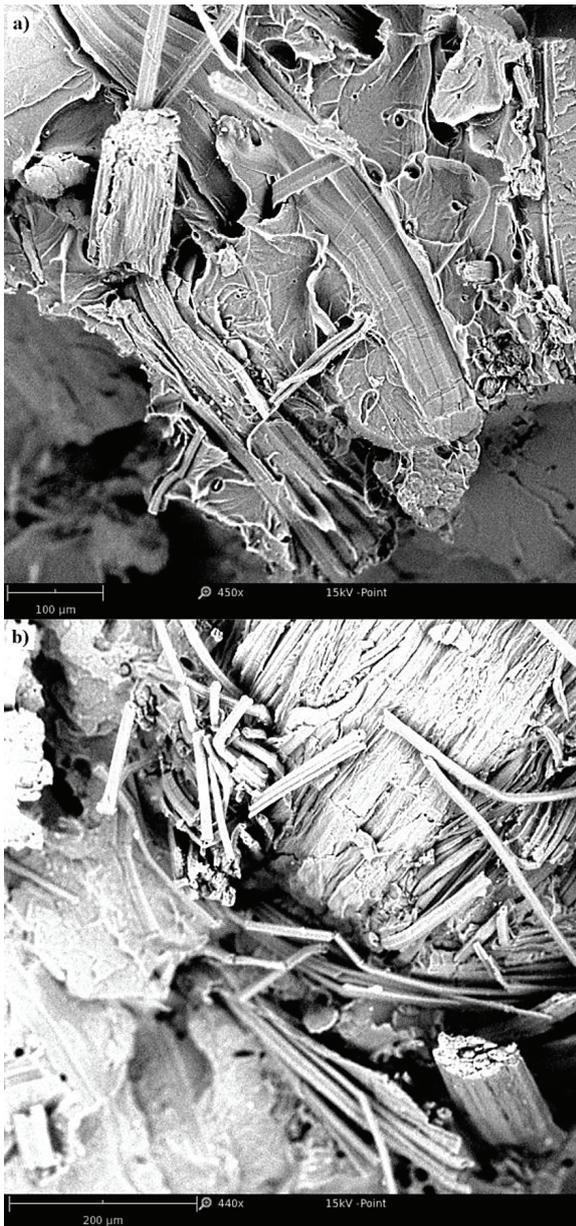


Figure 14. Morphology of the specimen with 3% linen fiber content: a) before degradation b) after degradation

The tests of mechanical properties showed that the addition of linen fibers increases the stiffness of the composite (Young modulus). Higher stiffness for samples containing linen fibers is observed both before and after degradation. The other tested values, i.e. tensile strength and elongation at break, decreased with increasing content of linen fibers. This may be due to the uneven distribution of fibers in the measuring part of the sample. There is a higher concentration of fibers in the gripping part of the samples. In summary, adding natural fibers to PLA made it possible to

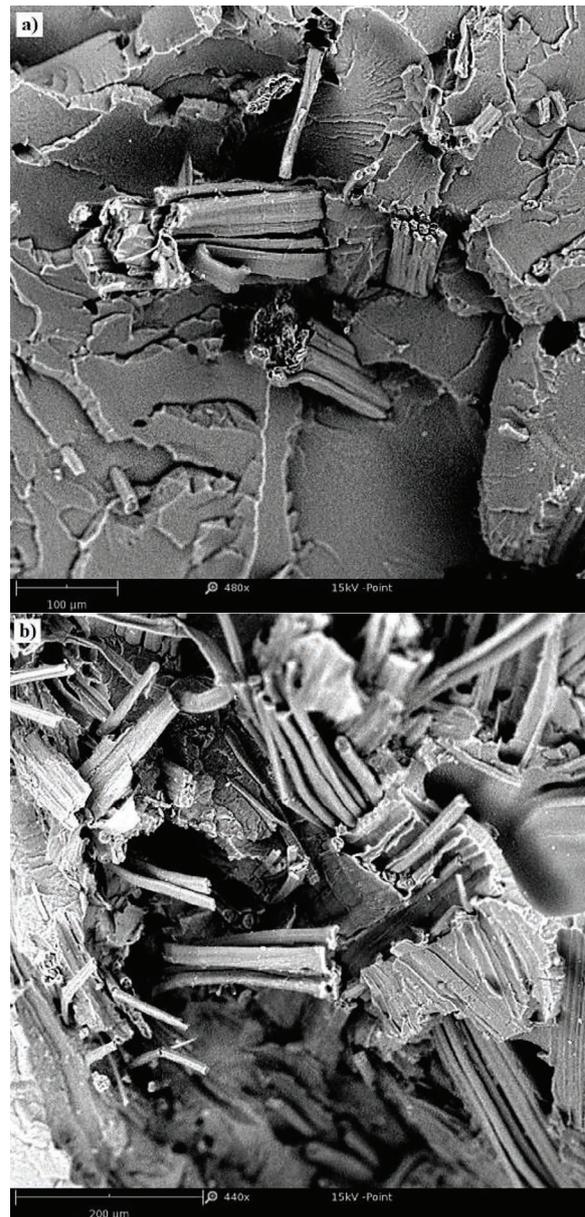


Figure 15. Morphology of the specimen with 4% linen fiber content a) before degradation b) after degradation

obtain a fully degradable biocomposite. However, it is necessary to verify the amount of added fibers and the method of processing the composites so that the selected properties, especially mechanical ones, was satisfactory.

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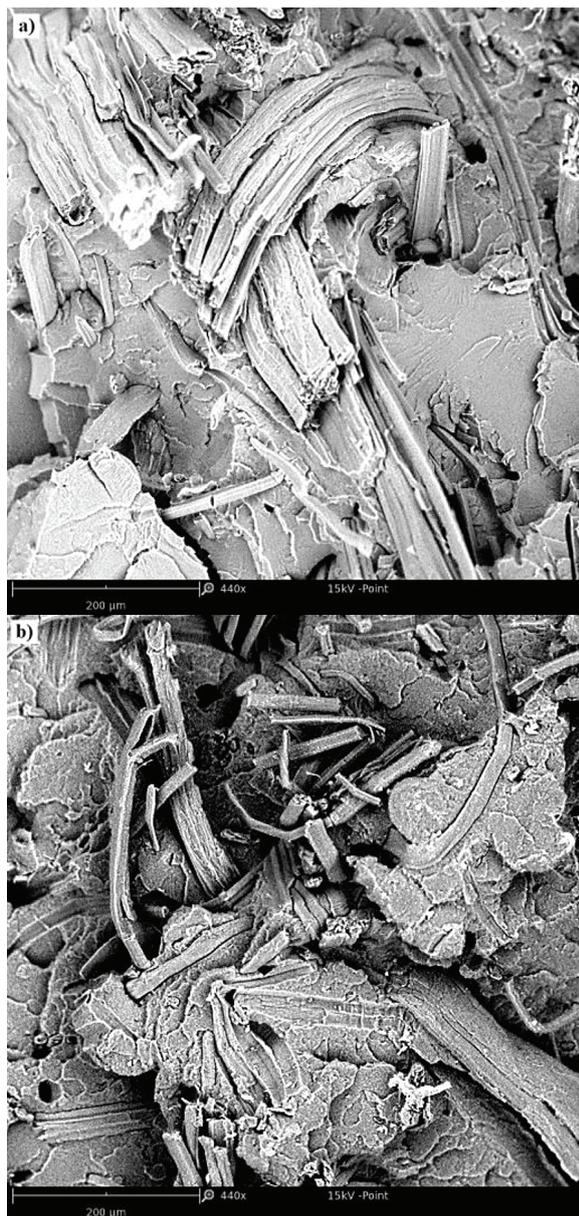


Figure 16. Morphology of the specimen with 5% linen fiber content: a) before degradation b) after degradation

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