The composting of PLA/HNT biodegradable composites as an eco-approach to the sustainability

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Abstract. The article presents the results of research related to the decomposition of polylactic acid (PLA)/halloysite nanotubes (HNTs) biocomposites into a simple organic form. After completion of the nanocomposites manufacture, the evaluation of the composting process simulation was conducted using the biodegradation method. First, the selected properties of PLA/HNTs biocomposites, such as density, water absorption, and impact strength were tested. Next, the impact of the composting process from 30 to 90 days on the behavior of PLA/HNTs composites was investigated. Finally, the loss of mass of the composites, hardness, and the structural changes of the biocomposites under the composting conditions before and after the composting were evaluated using SEM microscopy. The results showed, that the PLA modified by HNT particles has the properties to biodegradation process friendly and therein fully suitability for organic recycling. Due it means, that in the coming years may contribute to the replacement of non-biodegradability polymers, i.e. polyolefins and polystyres, and reduction of plastic packaging wastes.

Key words: polymer composite materials (PMC), biocomposites, polylactic acid (PLA), halloysite, composting process, performance properties

1. Introduction

Polymer materials constitute the majority of common materials used for housings of household appliances, packaging, as well as materials used in the automotive, medical, and other sectors [1–2]. They have the desired features, such as low mass, often high transparency, and above all, they are easy of forming and colors and cheap in production. However, the increased use of polymers has led to serious environmental problems due to their complete non-biodegradability [3–5]. Although complete replacement of the polymers with environmentally friendly biopolymers is simply impossible to achieve. Hence, the use of biodegradable polymeric materials, including biocomposites should be the future in specific applications such as medical and dental accessories and food packaging [6]. In numerous parts of the world, the processing of biodegradable polymers by composting is now considered an appropriate form of material recovery. In the UK, it is a permissible recovery option under the producer responsibility legislation (packaging waste) [7–8]. In other countries, Poland included there are programs intended for environmental protection and limiting the use of petroleum polymers. After the Regulation of the Polish Minister of the Environment of May 25 2012 on the reduced levels of the weight of biodegradable municipal waste sent for landfililing and the method of calculating the reduced levels of the weight. The municipalities are obliged to limit the weight of municipal waste sent for landfill to 35% of the total mass of the biodegradable municipal waste. Therefore, the goal of numerous countries is to strive towards the utilization of the largest possible group of used products through biodegradation. Recyclable biocomposites based on degradable polymer matrices and natural fillers such as cellulose, starch, flaxen, hemp, and wood are desirable in a sustainable society due to their more favorable properties and shorter decomposition period.

The fillers of natural origin also include halloysite [9], which is used as a raw material in the ceramic industry, for the production of mineral sorbents, as a feed additive, and as a catalyst for filter beds. Hence, the production of composites with biocompatible fillers is advantageous, mainly due to their easy biodegradation [10–13].

In accordance with ASTM D996 standard [14], the biodegradable polymers must "demonstrate the ability to biodegrade under certain assumptions in the composting environment, so that the decomposed polymers are not visually distinguishable and decompose into carbon dioxide, water, inorganic compounds, and biomass, at a rate consistent with known compostable materials, e.g. cellulose. The first stages most often include abiotic, such as temperature, light, atmospheric pressure, air and/or soil humidity and biotic, i.e. bacteria, fungi, etc. processes. The purpose of which is to degrade the polymer to a low molecular weight form under suitably favourable conditions. And the resulting fragments of polymer or polymer composite decay must be completely used up by microorganisms. Otherwise, it can be a potential for negative environmental and health consequences [15].

Products from an industrial composting process, which is usually 12 weeks with a temperature above 50°C must meet quality criteria, such as regulated heavy metal content, ecotoxicity, and lack of visible, distinguishable polymer residue [16–18].
Composting has the potential to transform biodegradable waste, including biodegradable plastics, into useful soil improvement products [19]. For example, the decomposition of polymers by composting combines the influence of ester bonds hydrolysis with the activity of enzymes [17, 20-22]. However, the composting process requires the presence of specific compounds, i.e. carbon, nitrogen, oxygen, water [1, 10, 17, 23]. Knowns, that a crystalline structure PLA is more resistant to degradation than an amorphous structure PLA and that the degradation rate decreases with an increase of the degree of crystallinity [23–25]. The degradation of polymers depends also on their molecular weight, and in the case of polymers, the degradation rate decreases with an increase in their average molecular weight [26]. While the higher the melting point of polyester, the lower is the degradation tendency to enzymatic degradation [26].

Li and McCarthy [27] the effect of stereoisomeric PLA content on the degradation rate of PLA membranes using proteinase K were investigated. They reported that the initial degradation took place at the surface and that the degradation rate increased with an increase of L-lactate unit content. Similarly, the degradation of lactidoligomers with dimers and lactic acid monomers with different stereoforms using Fusarium moniliforme and Pseudomonas putida were studied. The results reported that the low molecular weight oligomers were completely degraded regardless of their enantiomeric composition. The L-dimer was quickly consumed while the racemic oligomers were slowly assimilated [10].

The authors of several papers [21, 28, 29] on the subject emphasized the validity of polylactide degradation by the composting process. Soil burial tests show that the degradation of PLA in the soil is slow and takes a long time to start, and after 6 weeks in soil, degradation wasn't observed on PLA sheets [29]. Urayama and Kanamori [30] reported that the molecular weight of PLA films of different optical purity of the lactate units (100% L and 70% L) decreased by 20 and 75%, respectively, after 20 months in soil. On the other hand, PLA can degrade in the composting environment, where it is hydrolyzed into smaller molecules such as oligomers, dimers, and monomers. Next, these smaller molecules are then broken down into carbon dioxide (CO₂) and water (H₂O). The microorganisms contained in the compost pile break down organic waste by using the carbon contained in it as an energy source and building its nitrogen into the cell structure, therefore transforming materials into carbon dioxide, mineral salts, and water [1, 8, 10].

In the case of the composites, the biodegradation process is similar to that of the biodegradable polymers and largely depends on the decomposition conditions [31–32]. Gil-Castell determined the biodegradability of polylactide-based monomer composites [31]. They found that the synergistic combination of water and temperature with compost plays a key role in the biodegradation process of the materials [31]. Giri and Badia [32] found that composite with cellulose filler, at completely degraded within a few months of composting in soil and showed high water absorption and that these properties were additionally enhanced by the filler. Compared to the pure copolyester of adipic acid, 1,4-butanediol, and terephthalic acid (from dimethyl terephthalate) - PBAT, the composites showed increased hydrophilicity of the surface, which has increased their degradability. Olsén and Herrera [33] showed that the poly (ε-caprolactone) matrix undergoes a localized heterogeneous polymer degradation in the area of the cellulose fiber-matrix interface during mixing in the melted state. The degree of local degradation correlates with the initial moisture content in the wood cellulose fiber [33–35]. As a result, the high moisture content causes a destabilized and degraded fiber-matrix interphase.

The literature review presented above shows that it is advisable to produce polylactide-based biocomposites with additional strengthening in the form of halloysite nanotubes and to subject them to the composting process in laboratory conditions.

The aim of the paper the properties selected of new biodegradable polymeric materials, such as density, water absorption, and impact strength were examined. And finally, the evaluation of the composting process at a duration of 1 to 3 months on the behavior of the biocomposites based on changes in a loss of mass sample and hardness as well surface morphology with microscope observations was evaluated.

2. Experimental

2.1 Materials

The nanocomposites were produced using a polylactide by NatureWorks (Minneapolis, Minnesota, USA) under the trade name Ingeo™ Biopolymer 3260HP as the matrix material [36]. The polylactide is characterized by an amorphous structure with MFR = 65 g/10 min (210°C; 2.16 kg), tensile strength ca. 63 MPa, elongation of 3% and linear contraction of 0.2 - 0.4%.

Halloysite (nanotubes) in the form of powder by Sigma-Aldrich [37] was used as the nanofiller. The material has the following properties: size d x L: 30 - 70 nm × 1 - 3 μm, refractive index: nD = 1.54, pore size: 1.26-1.34 ml/g, the surface of the nanotube: 64 m²/g and density: 2.53 g/cm³ [37].

2.2 Nanocomposites processing.

The process of producing the nanocomposite initially consisted of a modification of strengthening the phase with a natural polymer - gelatin. This procedure was dictated by the desire to obtain a nanocomposite of an even distribution of the filler in the matrix and resulted from the authors' own experience in the field [38].

The modification was made on the basis of the operation of an ultrasonic field of a 250 kHz frequency in a demineralized water environment with the mass ratio of gelatin to halloysite equal 1:2. The process was carried out
at a temperature of 80°C for 3 hours. After the reaction was complete, the water was removed by evaporation, and the dry product was used to produce a fine, loose powder, which was then ground in two stages: preliminary grounding in a knife mill, then grounding in a ball mill. Halloysite modified with a natural polymer was introduced into the polylactide by dosing the nanopowder in the injection process in a pre-dispersed form in a polymer carrier (masterbatch), which facilitated the production of a composite with a good dispersion of the filler in the polymer matrix. The research material was produced using the Laborextruder LSM30 L/D 22.9, Leistritz (Nürnberg, Germany). Before the extrusion, the granulate was dried in a dynamic vacuum (70°C, 12h). The extrusion temperature equaled 200°C, the screw rotation speed was 50 rpm, and the extrusion capacity was equal 1.5 kg/h. The test fittings were manufactured using an injection molding machine by Dr. Boy GmbH & Co with a mold closing force of 15 tons (Neustadt - Ferntahl, Germany). Injection process parameters were as follows: plasticization temperature 200°C, the injection pressure was about 50 MPa, and the holding pressure was about 41 MPa. At these parameters, composites of 1 wt.%, 2.5 wt.%, and 5 wt.% halloysite in the polylactide matrix weight were produced. The paper conducted an analysis of the materials in accordance with Table 1.

### Composting process.

In order to assess the degree of degradation (the study of material decomposition over time) of the produced nanocomposites, a composting process was carried out. The study of the decomposition of bio-composites over time was carried out in laboratory conditions simulating composting in an industrial pile. The conditions in the pile cause interactions between the different stimuli causing the degradation of the material. This enables conducting research on the degradation of composites via the shortened degradation method. The composting process was carried out in a substrate consisting of 30% leaves, 20% wood chips, 30% grass, 10% soil, and 10% compost. The samples were placed in glass containers in a laboratory incubator so that the prism would cover them with a layer of min. 5 cm depth. During the composting process, changes in the temperature of the pile reaching a temperature of 72°C were observed, mostly in the first month of the process. The composting process was carried out at an average temperature of 52°C, the relative humidity of 55%, and a pH of 6.7. The time of accelerated composting in the compost pile lasted 3 months (Fig. 1).

### 3. Characterization

Surface morphology, density, water absorption, weight loss, and mechanical properties such as impact strength, hardness were evaluated. The morphology of samples using a scanning electron microscope (SEM) was investigated. In order to determine selected physico-chemical and functional properties as well as the structure of nanocomposites before the composting process and after the composting process for a period of 1, 2, 3 months. The shape and dimensions of the samples were prepared for all tests in accordance with the applicable requirements presented in [39–42]. The verification of the quality of the composting products and the assessment of their structure was carried out using macroscopic and microscopic tests. The authors of the study presented also an assessment of the viscosity-average molecular weight of the studied materials in [43]. Although this issue has a significant impact on the present study, it will not be presented here in favour of the authors referencing the final results of the study in the summary of the article.

#### 3.1 Properties of new biodegradable polymers.

During macroscopic studies, the flat surfaces of nanocomposites were observed with the naked eye or at a magnification of up to about 50 times (e.g. with a magnifying glass). Due to the magnification, it was possible to assess the surface structure, e.g. colour, separations, smoothness (topography), cracks, etc.

The density was determined using the hydrostatic method in accordance to the standard ISO 1183 - 1: 2013 [39]. The absorbency was carried out using the weight method, which was selected due to the greatest popularity in the literature [31, 38]. Moreover, it is recommended as

**Table 1. Materials used in researches**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Matrix</th>
<th>Reinforcing</th>
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<tbody>
<tr>
<td>PLA</td>
<td>polylactide</td>
<td>fraction (wt.): 100%</td>
</tr>
<tr>
<td>PLA+1% HNT</td>
<td>polylactide</td>
<td>fraction (wt.): 99%</td>
</tr>
<tr>
<td>PLA+2.5% HNT</td>
<td>polylactide</td>
<td>fraction (wt.): 97.5%</td>
</tr>
<tr>
<td>PLA+5% HNT</td>
<td>polylactide</td>
<td>fraction (wt.): 95%</td>
</tr>
</tbody>
</table>

**Fig. 1. Stages of the composting process (Own sources)**
an appropriate method for conducting this type of comparative research for a wide range of biodegradable polymeric materials. It should also be mentioned that this method is covered by the ISO 62: 2008 standard [41].

Initially, the sample was dried at 70°C for 24 hours, then it was cooled in a desiccator and weighed with 0.1 mg accuracy. The water absorption test was carried out in distilled water at 23°C for 10 ± 1 mm square samples. The samples were weighed at intervals of 30 minutes to observe the mass stabilization. The absorbency \(c\) was calculated using the formula (1),

\[
c = \frac{m_2 - m_1}{m_1} \times 100\% \tag{1}
\]

where: \(c\) is the water absorption [wt.%], \(m_1\) is the mass of the sample after drying [g], \(m_2\) is the mass of the saturated sample [g].

On the basis of the determined course of water absorption and the II Fick’s Law [44–45], the water diffusion coefficient was determined. If we assume that humidity and temperature have not changed, then the diffusion coefficient \(D\) of the board with infinitely large opposite surfaces directed towards the thickness of the composite is expressed by the formula (2):

\[
D = \pi \cdot \left( \frac{h}{4(M_m)} \right)^2 \cdot \left( \frac{M_1 - M_2}{t_1^2 - t_2^2} \right)^2 \tag{2}
\]

where: \(D\) is the diffusion coefficient, \(M_m\) is the water content which corresponds to the saturation state, \(M_1\) is the percentage of water absorbed in time \(t_1\) [s], \(M_2\) is the percentage of water absorbed in time \(t_2\) [s], \(h\) is the thickness of the sample [mm].

The impact resistance (brittleness) was determined by the Charpy method in accordance with ISO 179 - 1: 2010 [40], using the B 5102.201 pendulum hammer (Zwick/Roell, Germany), for the unnotched specimens with initial the potential energy 50 J.

3.2 Properties of biocomposite polymeric materials by composting.

Measurement of the loss of mass in the tested materials was carried out using the gravimetric method, which consists of measuring the mass and volume of the material sample, i.e. weighing and determining the volume by measuring linear dimensions with a caliper. The samples were tested before the composting process and after the composting process for a period of 1, 2, and 3 months. The materials were tested in accordance with Table 1.

Three samples from each material group were tested and the results were averaged. The hardness of biocomposites was measured using a Shore D hardness tester (Sauter HBD 100 GmbH, Balingen, Germany) according to the PN-EN ISO 868:2005 [46]. The surface morphology of PLA composites with addition of halloysite after the composting process was analyzed using a scanning electron microscope (Mira 3, TESCAN, Brno, Czech Republic) with high-resolution imaging. The microstructure analysis was performed for samples previously coated with a thin layer of a carbon powder (20 nm). The surface morphology of the biocomposites was investigated using the backscattered electron (BSE) signal and the secondary electron (SE) signal of an accelerating voltage equal 12 kV. A different range of magnifications was used in order to better visualize the analyzed structures.

4. Results and discussion

4.1 Microscopic analysis before and after composting.

Fig. 2 presents a comparison of the morphology of the pure PLA samples and its composites with the addition of HNT, before and after the 3 - month composting process. As shown, all samples underwent a partial degradation.

Fig. 2. A macroscopic view of pure PLA and its composites with different HNT content: a) before testing, b) after the 3 - month composting

Fig. 3-6 present the change in the surface appearance of the pure PLA (Fig. 3) and PLA+HNT composites (Fig. 4-6) during the composting process. It was observed for all materials that after 1 month of the composting the samples became cloudy, which is related to the hydrolytic degradation and an increase in brittleness of the materials [20].

In the further degradation process, yellowing and deposition of organic sediment, which is most likely a...
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Fig. 7. A macroscopic view of the PLA with 5 wt.% HNT composite surface after 3 months of composting with visible yellowing and organic sedimentation

4.2 Density analysis before composting.

One of the basic values characterizing the obtained material is its specific density. The dependence between the density and the percentage of the strengthening phase is presented in Fig. 8.

Fig. 8. Density of pure PLA and its composites with different HNT content before composting

Fig. 8 shows that for the produced nanocomposites, the greater the strengthening phase, the higher the density of the tested materials. The addition of 1 wt.% HNT nanofiller to the PLA matrix increases the density by 4%, while the addition of 5 wt.% HNT increases it by about 8%. This increase results from the higher density of the introduced filler, which is a halloysite nanotube (density approx. 2.2 g/cm³), as compared to the matrix material made of polylactide.

4.3 The results of the water absorption biocomposites before composting.

Fig. 9 presents the results of determining the water absorption of the produced nanocomposites and of the pure PLA. As can be noted from the obtained results, the increase of the HNT nanofiller content strengthening the PLA matrix results in a water absorption increase, which has also been observed by co Russo and Cammarano [47]. The addition of 1 wt.% HNT increases the water absorption by 60%, and the addition of 2.5 wt.% HNT reinforcement increases the water absorption by up to 3 times compared to the pure matrix material.
This tendency is also confirmed by the results of the water diffusion coefficient (Fig. 10), which is caused by capillary flow to the nanotube/matrix boundary layer and possibly an increase in the microporosity of the material in the presence of the nanotubes. It is also impacted by the hydrophilic nature of the nanotubes [48-49]. HNTs are characterized by a large developed surface and a high proportion of hydroxyl groups which contribute to the rate of water absorption [50].

While observing the change in mass increase related to the water absorption of the tested material over time, it can be noticed that for all tested materials the greatest changes (Fig. 11) take place in the first stage of the process and then in the saturation stage. This indicates that the water absorption behavior of the PLA composites is consistent with Fick's second law defining the prediction of the effect of diffusion on the change in the local concentration over time [45, 48]. Thus, water absorption is related to its rate of diffusion into the composites. This is caused by the easier diffusion of water molecules in the first study stage.

Water molecules penetrating the material can cause changes of its physical - reversible, or chemical - irreversible - nature. In the initial phase, with intermittent exposure in a humid or water environment, it is possible that only physical changes occur, which are then manifested by the swelling of the polymer matrix due to the increase of intermolecular spaces by water molecules.

However, the chemical bonds of the nanoparticle - matrix are not broken; therefore, the observation of the surface of the samples before and after the water absorption test shows no significant changes in the color and texture of the observed samples (Fig. 12).

In order to determine the leaching range of the HNT nanotubes of the PLA+HNT composites, during the assessment of water absorption the samples were dried again and the weight loss of the composites was determined (Fig. 13). In all cases, a slight weight loss of the PLA composites (max. 0.08%) was observed. The loss of mass is most likely caused by the leaching of the HNT particles on the surface of the sample, which nonetheless was not confirmed by the macroscopic observation.
4.4 Impact strength analysis before composting.

The results of the impact test of PLA with HNT composites are presented in Table 3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Impact strength [kJ/m²]</th>
</tr>
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<tbody>
<tr>
<td>PLA pure</td>
<td>146 ± 50</td>
</tr>
<tr>
<td>PLA+1 wt.% HNT</td>
<td>128 ± 21</td>
</tr>
<tr>
<td>PLA+2.5 wt.% HNT</td>
<td>131 ± 15</td>
</tr>
<tr>
<td>PLA+5 wt.% HNT</td>
<td>116 ± 25</td>
</tr>
</tbody>
</table>

It was found that the pure PLA had the highest impact strength, and the addition of the halloysite nanotubes caused a decrease in the impact resistance. This is in line with the common theory that the impact resistance value is low for "brittle" materials and high for ductile materials [51]. The addition of ceramics in the form of halloysite causes this exact brittleness of the material. Debonding, pull-out, and fracture of the fibers are the three mechanisms of energy absorption during impact. It is assumed that the strain energy which is released by particles debonding and fracture is proportional to the debonded length. Consequently, poor adhesion between matrix and fibers leads to higher energy absorption [52]. Thus, the better particles/matrix adhesion in the PLA/HNT composite could be an explanation for the worse impact strength compared to pure PLA. The decrease in the impact strength of the composite materials may also be connected to a certain heterogeneity of the composite, as indicated in the literature [53–54].

The presence of the HNT agglomerates resulted in poor quality material. Due to the differing characteristics of the matrix and nanotubes, the HNT located in the structure of the material acts as an inciter of the initiation and growth of cracks, thus leading to a clear brittleness homogeneity and causing a decrease in the impact resistance of composites containing it.

4.5 Mass loss at time analysis of biocomposites before and after composting.

An assessment of the weight loss of the tested nanocomposites after the composting process was carried out after 1, 2, and 3 months, as presented by Fig. 14.

All materials showed an incubation time of about 30 days, during which there was a slight weight loss between 1 and 5%. The pure matrix material shows the greatest weight loss, which is confirmed by the literature data as well [43, 51, 54–56]. After the 1-month period, the rate of disintegration increased. The decomposition of the PLA was directly related to the hydrolytic degradation of ester groups, therefore it is important to control the composting parameters, i.e. temperature and humidity. After 2 months of composting, the greatest degradation was still shown by the pure PLA; however, the weight loss increased to 6% for the PLA with 1 wt.% HNT composite. After 3 months of composting, all composites showed approx. 10% weight loss.

On the basis of the conducted research, it can be concluded that the participation of HNT causes a delay in the degradation process, which is manifested by a lower weight loss after the same period of time as compared to the pure PLA, since the halloysite did not degrade due to its inorganic nature. However, as shown by the authors in [43], the addition of a halloysite promotes the breakdown of the polymer matrix.

As a result of 1 month of composting, a decrease in the viscosity-average molecular weight by 23% for the pure PLA and approx. 25% for the composite containing 5 wt.% HNT was observed. The greatest decrease in the viscosity-average molecular weight was shown by a sample containing 5 wt.% HNT composted for 3 months [43].

4.6 Shore hardness analysis of biocomposites before and after composting.

Assessment of the hardness of the PLA/HNT nanocomposites using the Shore method before the composting process and after the composting process carried out after 1, 2, and 3 months is presented in Fig. 15.
Fig. 15 presents the Shore hardness results of all composites, as compared to the pure PLA before the composting process. The research shows that adding HNT to the PLA matrix increased the hardness for all PLA+HNT composites from 83°Sh to about 87°Sh. In the case of 1 wt.% HNT, the hardness increased by approx. 2.5%, and for the 5 wt.% HNT - by 5.4%. After 1 month of degradation, there was a slight decrease in the hardness of all composites. Figure 15 shows that in the case of the PLA matrix, the hardness dropped by 4.3% after 3 months of composting. In the case of the hardness after 3 months of composting, it can be observed that for the PLA+5 wt.% HNT composite the decrease in hardness equalled 4.4%. This proves that the addition of nanofiller, despite causing a delay in the process of decomposition of the PLA with HNT nanocomposite in relation to the PLA polymer matrix itself, increases the disintegration of the polymer matrix, which is confirmed by the results of the viscosity average molecular weight in the paper [43].

At the first stage of composting, the process responsible for the systematic reduction of the average molecular weight of the samples is the hydrolysis process of polylactide, and the formed small-molecule oligomers penetrate into the environment, wherein the second stage they are bio-assimilated by the microorganisms present there.

In the initial stage of degradation of composites, water penetrated into PLA, leading to hydrolytic cleavage of PLA ester bonds, leading to a rapid decrease in average molecular weight. This decrease in molecular weight allowed for the creation of crystalline structures among the short chains of PLA, and therefore the crystallinity of PLA increased at once in the first step, which is shown in the turbidity of the sample.

As a result of composting for 1 month, a decrease in average molecular weight was observed by approx. 23% for pure PLA and about 25% for a composite containing 5 wt.% HNT. The result found the highest decrease in average molecular weight for a sample containing 5 wt.% HNT composted within 3 months was conducted.

4.7 SEM microstructure of biocomposites before and after the composting.

In order to assess the degree of the biodegradation, the structure of the pure PLA and its PLA composites of various HNT content was observed using the SEM technique. Fig. 16-17 present the surface of the biopolymers before and after 3 months of composting of the pure PLA and its PLA+5 wt.% HNT, respectively.

Fig. 17 shows the clear differences in the surface morphology of the composites depending on the nanotube content in PLA.
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Following that, Fig. 18 also illustrates the effect of composting time period (1, 2 and 3 months) on the surface morphology of composites with 1 wt.% and 5 wt.% HNT content.

In the case of composites with 5% content of HNT, a significantly higher increase in the brittleness of the material is visible, as compared to the composite with less HNT. Moreover, the composting time significantly influences the decomposition process of the composites. After 90 days of composting, there was a significant disintegration of the sample surface, especially in the case of the PLA with 5 wt.% HNT composite (Fig. 18f). Additionally, Fig. 19-20 shows the significant changes of these surfaces for the PLA composite with 5% nanotube content subjected to the composting process, with clearly marked effects of partial biopolymer decomposition.

The presented research on the microstructure clearly shows that the composite materials degraded in the composting process (Fig. 16-21). The biodegradation initially manifests as an increase in the fragility of the sample, then in the form of transverse cracks, delamination visible on the sample surface, as well as the separation of the surface layer from the sample substrate (Fig. 19). In the case of nanocomposites, the formation of crack propagation was observed in the presence of agglomerates or the HNT nanotubes themselves (Fig. 20), which promotes faster destruction of the material by disturbing the nanocomposite substrate and creates a greater possibility of depositing bacteria, microorganisms contained in the soil, or other factors affecting the decomposition of the biocomposite.
5. Conclusions

The article assesses the properties and degree of degradability of the PLA/HNT biocomposites. The paper involved the production of biocomposites with a content of 1 wt.%, 2.5 wt.% and 5 wt.% HNT in the PLA matrix. Next, the effect of the HNT content on the mechanical and functional properties and degradation of new biomaterials was determined. The results showed that the mechanical properties of the manufactured biomaterials were slightly lower than in the case of the pure PLA, but the decrease in impact resistance amounted to a maximum of approx. 20%, which was a positive effect. The PLA/HNT composites are characterized by a higher water absorption than the pure PLA due to the presence of the HNT nanotubes which show a strongly hydrophilic character [9]. The increase in the water absorption has a negative effect on the products used in the maritime industry, but in the case of medical applications as a carrier of drugs, the PLA/HNT biocomposite may prove to be an ideal solution.

The results of the research show that all tested materials are subject to the degradation process, but nevertheless, with the increase in the content of HNT nanoparticles, the degradation rate of the PLA/HNT composite was lower, which was caused by the presence of non-degradable nanoparticles. The addition of halloysite promotes the breakdown of the polymer matrix [35]. This tendency is confirmed by the results of the Shore hardness. After 3 months of composting in the case of the PLA matrix, the hardness decreased by approx. 4% and 5% for the PLA with 5 wt.% HNT added. At the beginning of the composting process, the greatest weight loss noted for pure PLA. During the process, the rate of disintegration increased, so it is important to control the composting parameters, i.e. temperature and humidity. After ending composting, all biocomposites showed approx. 10% weight loss. As a result of composting, a decrease in the viscosity-average molecular weight [43]. The results of the viscosity average molecular weight showed that as a result of composting all materials are degraded. As a result of composting for 3 months, a decrease in viscosity-average molecular weight was observed by approx. 20% for pure PLA and about 25% for a composite containing 5 wt.% HNT. The viscosity found the highest decrease in average molecular weight for a sample containing 5 wt.% HNT, composted within 3 months was conducted [43].

The analysis of microstructure research clearly indicates the biodegradation of the materials after the composting process, which is shown by increased fragility, cracks, and delamination on the surface. This is most visible for the PLA/5 wt.% HNT composite. Overall, the research results showed that the PLA/HNT composites open up new options of application in medicine, where they can be used as carriers for controlled drug delivery, as well as of the production of single-use packaging, as would allow being disposed of with other organic waste in the composting plants.

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