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Physicochemical Assessment of the Biodegradability of Agricultural Nonwovens Made of PLA

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Abstract

Compostable biodegradable plastics are an ecological alternative to traditional products based on petroleum derivatives, whose post-use waste may pollute the natural environment. Modern polymer materials show the functional properties of plastics obtained by conventional methods, but they also may be degraded as a result of biochemical transformations in composting. This allows such materials to be included in the scheme of the currently implemented circular economy, which does not generate post-consumer waste. This paper presents methods for the assessment of the biodegradation process of selected agricultural nonwovens produced from commercial PLA 6252D polylactide, supplied by Nature Works® LLC, USA. The agricultural nonwovens tested, obtained by the spun-bond technique, were characterised by different degrees of crystallinity in the range from 11.1% to 31.4%. Biodegradation tests were carried out as simulated aerobic composting while maintaining constant environmental conditions in accordance with test procedures based on PN-EN/ISO standards using the method of sample mass loss determination. Gel chromatography (GPC/SEC) and FTIR spectroscopy were also applied to assess the degree of biodegradation. The aim of this study was to evaluate the effect of the crystallinity of nonwoven made of PLA 6252 D on its degradation in a compost environment.

Key words: *PLA agricultural nonwovens, degradability, compostability, GPC/SEC, FTIR.*

Introduction

Environmental pollution is one of the major problems of the world today. Increasingly, people have to deal with waste constituting persistent organic pollutants, which often end up in the environment as post-consumer waste [1].

Since the obtainment of the first synthetic polymers, technology has been focused on the development of synthesis methods for the production of improved plastics that would be characterised by good performance, high durability, and by resistance to physical and chemical factors as well as environmental conditions. In recent years, however, due to the increasing amounts of post-consumer polymeric waste in landfills, and thus a growing problem with the management of plastic waste, many scientists have begun research on obtaining new biodegradable polymeric materials [2, 3].

Following the idea of sustainable development, technologies for obtaining modern polymers are being developed, which will contribute to the improvement of living standards and the protection of the natural environment. These technologies cover the entire product life cycle, from manufacturing processes through its use to the final stages of recycling and utilisation [4]. The solution to the current problem is to replace traditional products based on petroleum derivatives

with polymer materials which will be derived, among others, from plant products such as corn or soybean [5, 6]. Such modern materials, called "double-green polymers", should show useful properties comparable to conventional plastics, but at the same time should be degradable through biochemical changes, e.g. as a result of composting, without posing a threat to the natural environment [2, 7-9].

Currently, in many industries e.g. in agriculture, the packaging industry and textile industry, non-degradable plastics are being replaced with environmentally friendly polymers. The introduction of biodegradable materials for everyday use can contribute to a reduction in the huge amounts of solid waste generated, whose recycling is unprofitable and/or impossible [10-12].

Available data indicate that the global production of bioplastics in 2019 amounted to 2.11 million tonnes, and according to forecasts, in 2024 it will reach the level of 2.43 million tonnes. Most of the production is consumed by the packaging sector, but also the agro-textiles market is an important recipient of bioplastics [13, 14]. In the group of biodegradable bioplastics, poly (lactic acid) is very important nowadays. Polylactide technology consists in corn starch fermentation, form which lactide is obtained, which next, in the presence of a catalyst, is con-

verted into polylactide (PLA). PLA is a completely degradable, linear aliphatic polyester showing both good physico-mechanical and physico-chemical properties [15-17]. The global production of PLA in 2019 amounted to 13.9% of the total bioplastics production, which is second to starch (21.3%) [39]. This is due to the great interest of the R&D sector in new bioplastics. Polylactide is currently the subject of many research works both at the application and implementation level. It is recognised as one of the materials constituting an alternative to polymers derived from crude oil, which will reduce the consumption of this raw material and reduce the burden on the natural environment [18].

Currently, Nature Works® LLC is a leader in the technology of obtaining biodegradable polymers, including polylactide. In recent years, Nature Works® LLC has carried out work on the development of products based on lactic acid derivatives that may be used for the production of plastics, packaging and in specialised fibrous applications [19].

Products formed from polylactide are used, among others, in agriculture as a fibrous material for mulching the soil around plants, for covering tunnels or for the production of plant pots. The application of such products enable producers to obtain larger and earlier crops, making fruit production independent of environ-

mental conditions, allowing to reduce the use of insecticides, and contributing to the better use of nutrients and water by plants [20, 21].

Nonwovens made of PLA 6252D polymer by the spun-bond method at the Polymers and Synthetic Fibres Department of Łukasiewicz-IBWCh are an example of innovative products for agricultural use which after finishing their life cycle may, as a waste, be further broken down through the aerobic composting process into simple compounds (CO_2, H_2O) and biomass which have no toxic impact on the natural environment. Composting, the oldest method of managing biodegradable waste, eliminates the problem of waste removal by other methods and, at the same time, creates the possibility of obtaining significant quantities of a valuable natural fertiliser [22]. Maintaining proper humidity and temperature conditions of the compost substrate enables the development of microorganisms, partial degradation of compost constituents and transformation of organic matter into humus compounds [23]. The aerobic microorganisms that colonise compost multiply on the surface of the polymer material subjected to the composting process and adapt to the new conditions, producing enzymes in their cellular structures that are secreted outside the cells, allowing polymer degradation.

Such degradable materials readily undergo hydrolysis and/or oxidation reactions which are catalysed by enzymes. As a result of this process, low molecular weight metabolic products (monomers, dimers) are formed [24, 25].

The enzymes involved in the degradation of aliphatic polyesters are proteases and lipases, which recognise and cleave PLA α-ester bonds [7, 26].

Enzymatic activity in compost depends primarily on the increase in the population of microorganisms that secrete extracellular enzymes involved in biological degradation. It is known that in compost there is a large population of thermophilic bacteria, actinomycetes and fungi [34]. To date, many literature data have shown the ability of various microorganisms to degrade PLA. These include strains of the genera *Bacillus, Geobacillus, Aneurinibacillus, Amycolatopsis, Cladosporium, Thermoactinomyces, Thermopolyspora, Stenotrophomonas* and *Pseudomonas* [27].

Table 1. *Physical-mechanical parameters and crystallinity degree of PLA agro-nonwovens.*

Sample marking	Area density, g/m²	Thickness, mm	Fibre diameter, µm	Crystallinity degree, %
37/12/2	56.6	0.32	9.56	11.1
37/12/4	56.9	0.32	8.97	21.7
37/12/6	53.8	0.30	8.94	31.4

The activities of enzymes, thermophilic bacteria, actinomycetes and fungi responsible for the breakdown of organic matter depend on many external and internal factors that can synergistically accelerate or inhibit the process of polymer degradation. For example, too high or too low temperature and unfavourable pH may inhibit microbial growth, but, in turn, adequate water content facilitates the migration of microorganisms present in an inoculum. Other factors affecting the rate of the biodegradation process are, among others, the chemical structure of the PLA polymer and processing conditions during the production of test materials [16].

The purpose of this work was to continue research on the assessment of the susceptibility of nonwoven products made from PLA 6252D (Nature Works® LLC) to biological degradation caused by aerobic microorganisms present in the compost and on determination of the impact of crystallinity of the nonwoven tested on the degradation process. The research involved physicochemical assessment of nonwoven products at individual stages of the composting process.

The test results obtained allowed for an examination and thorough analysis of the kinetics of PLA agro-nonwoven degradation.

Three PLA nonwovens with different degrees of crystallinity were subjected to the decomposition process. Degradation tests were performed in laboratory conditions simulating the aerobic composting process by the mass loss determination method based on standards [28-30].

■ Materials and methods

Degradation tests were carried out on nonwoven materials made of poly (D, L-lactide) 6252D from Nature Works® LLC (USA). The polymer characteristics, according to the manufacturer's data and results of its degradation tests in a compost environment, are presented in article [16].

In order to implement the research assumptions, three nonwovens of significantly different crystallinity were selected, but also with other very similar parameters, as shown in **Table 1**.

Agro-nonwovens designated as 37/12/2, 37/12/4 and 37/12/6 were selected for degradability assessment in laboratory composting conditions. Characteristics of the tests are presented in **Table 1**. The nonwovens were formed by the spun-bond technique at a calender temperature of 65 °C. In the forming process, various physico-mechanical parameters were used to obtain nonwovens with different degrees of crystallinity.

Forming of nonwoven materials

Nonwoven materials made of polylactide 6252D were formed of melted polymer by the spun-bond technique using a laboratory unit designed and built by "Polmatex-Cenaro" (Poland).

Conditions for forming the PLA agro-nonwovens were as follows:
- polymer melt temperature in the spinning head: 212 ± 1 °C,
- nonwoven fabric take-up speed: 2.9-6.8 m/ min,
- calender temperature: 65 °C,
- air temperature in the intake chambers: 14.7-16.5 °C,
- air pressure in the intake chambers: 1500 Pa,
- vacuum in the suction chamber, respectively: -512 Pa (nonwoven 37/12/2), -399 Pa (nonwoven 37/12/4), and -352 Pa (nonwoven 37/12/6),
- gap size in the forming channel, respectively: 9 mm (nonwoven 37/12/2), 13 mm (nonwoven 37/12/4) and 17 mm (nonwoven 37/12/6).

Decomposition tests[1)]

A study of the percentage weight loss of the nonwoven materials was carried out in a laboratory under aerobic conditions simulating the natural processes occurring during composting in accordance with the own Test Procedure: "Determination of the degradation degree of plastics and textiles by the mass loss determi-
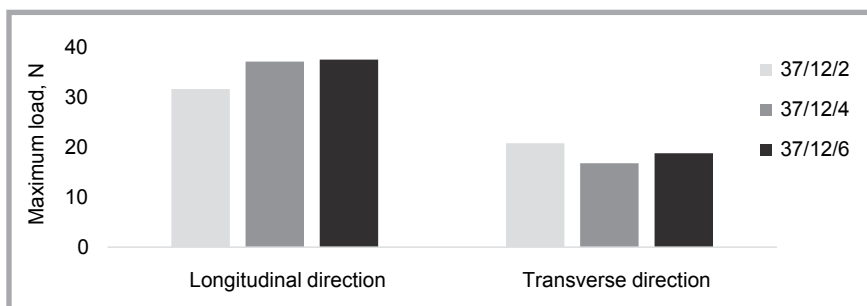
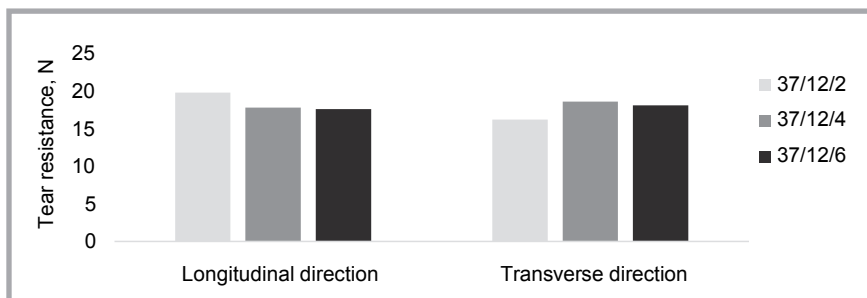**Figure 1.** *Determination of the breaking load for PLA agro-nonwovens.*

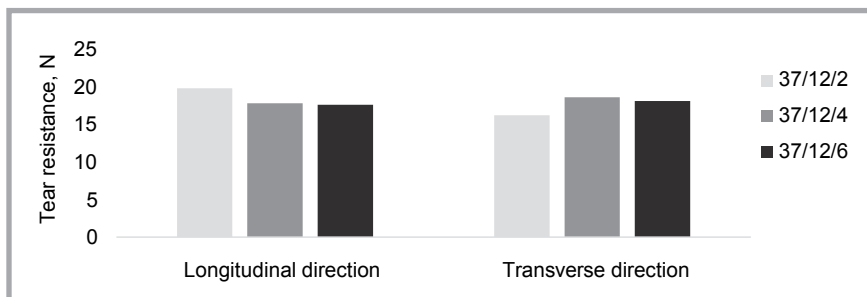**Figure 2**. *Determination of the tear resistance for PLA agro-nonwovens.*

Figure 3. *Determination of the elongation at break for PLA agro-nonwovens.*

nation method in simulated composting conditions on a laboratory scale", developed on the basis of the PN-EN/ISO standards regarding determination of the total biodegradation of polymer materials and textile products [28-30].

The test environment was compost at pH 7.0 originating from the Municipal Waste Management Company in Lodz, Poland, collected from a compost heap after a period of turbulent ripening. In the inoculum used, microbiological activity (total number of microorganisms) was determined in accordance with own Test Procedure [30] based on selected standards [31, 32], which was 1.6×10^8 cfu/g. According to the guidelines of the standards, the number of microorganisms present in the test medium should not be less than 1×10^6 cfu/cm³.

Properly prepared samples were incubated in a thermal test chamber under constant conditions at a temperature of 58 ± 2 °C and test medium humidity of 52.6%. The biodegradation process was monitored by removing individual samples from the inoculum at specified intervals, and then washing and drying to a constant weight. Then the relative weight loss was determined.

Assessment of biological activity[2] (total number of microorganisms)

Determination of the total number of microorganisms present in the compost environment was carried out according to the own Test Procedure: "Determination of the total number of microorganisms in compost and soil" [30].

Physical-mechanical tests[3]

Mechanical properties of the nonwoven were measured using an Instron 5544 tensile testing machine (UK), according to the PN-EN/ISO standards: Elongation at break, tenacity, in two directions (along and crosswise) [34], tear resistance [35], mass per unit area [36], thickness (using TILMED-64 apparatus, Poland) [37], fibre diameter (using LANAMETR MP2 apparatus, Poland) [38].

Physicochemical tests

Thermal analysis was carried out by means of Differential Scanning Calorimetry (DSC) using a Diamond (Perkin Elmer, USA). The first and second heating scan and cooling scan of the polymer were performed in the temperature range of $-70 \div 170$ °C. The samples were heated at a rate of 10 °C/min.

The crystallinity degree of the nonwovens selected was determined by DSC using the following *Equation (1)*:

$$X_C \ (\%) = \Delta H / H_{100\%} \cdot 100 \qquad (1)$$

Where, ΔH − difference between the enthalpy of melting and cold crystallisation, $H_{100\%}$ − enthalpy of melting for completely crystalline PLA (93.1 J/g) [47, 48].

The molar mass distribution and polydispersity[4] of both the polymer and nonwoven were analysed by the Gel Permeation Chromatography/Size Exlusion Chromatography (GPC/SEC) method. Tests were performed using the HP 1050 GPC system (Hewlett-Packard, USA). GPC/SEC analysis parameters are presented in article [6]. The average molar weights were determined using the universal calibration technique and the following values of the Mark-Houwink-Sakurada equation: for polystyrene (PS) a = 0.794, K = 0.0049 [39] and for PLA a = 0.759 & K = 0.0153 [40]. The Mw linear range for the Mixed C column used (Agilent, USA) is between 200 and 2 000 000 g/mol.

Fourier Transform Infrared Spectroscopy (FTIR)

IR spectra were taken using a Genesis Series FTIR equipped with specialised WinFIRST software (ATI Mattson, USA). The operating parameters were as follows: measurement range − 4000-500 cm⁻¹, resolution − 4.0 cm⁻¹, and the number of scans for the baseline and spectrum collection − 16. Samples for tests were prepared in the form of KBr tablets, with a concentration of 1 mg of the test sample in 300 mg KBr. The accuracy of wavenumber reading for characteristic bands was ± 1cm⁻¹.

Scanning Electron Microscopy (SEM) analysis

SEM investigation of the nonwoven was carried out using a Quanta 200 scanning electron microscope (FEI, USA). Tests were carried out on gold sputter coated samples in a high vacuum at an electron beam accelerating voltage of 5KV and magnification of 500x.

■ Results and discussion

Characteristics of PLA agro-nonwovens with different crystallinity produced by the spun-bond technique and subjected to the decomposition process in a compost environment

The results of research on PLA 6252D polymer in regard to its thermal properties, molecular characteristics, including determination of average molecular weights, and assessment of physicochemical properties, including determination of parameters such as inherent viscosity, ash content and acidic groups content are presented in the previous article [16].

Samples of agro-nonwoven marked as 37/12/2, 37/12/4 and 37/12/6 were tested in terms of GPC/SEC chromatography, DSC thermal analysis as well as physical and mechanical characteristics in order to investigate the mechanism and kinetics of the disintegration process during the degradation process.

Physical-mechanical parameters of the samples tested are presented in *Table 1* and in *Figures 1-3*.

Analysis of the breaking force and elongation of the nonwoven samples in a direction parallel to the forming direction (longitudinal direction) showed an effect of the crystallinity degree on the increase in strength. while in the tests performed in a direction perpendicular to the forming direction (transverse direction), no effect of the degree of crystallinity on nonwoven strength was found. For the 12/37/2 nonwoven slightly better strength parameters were obtained in the transverse direction, which may be due to the larger diameter of fibres and the area density. Probably, during nonwoven forming in the spun-bond process, the fibres emerging from the spinneret become much better oriented in the longitudinal direction (*Table 2*).

Figure 4. Effect of the duration of the biodegradation process on the mass loss of PLA agro-nonwovens.
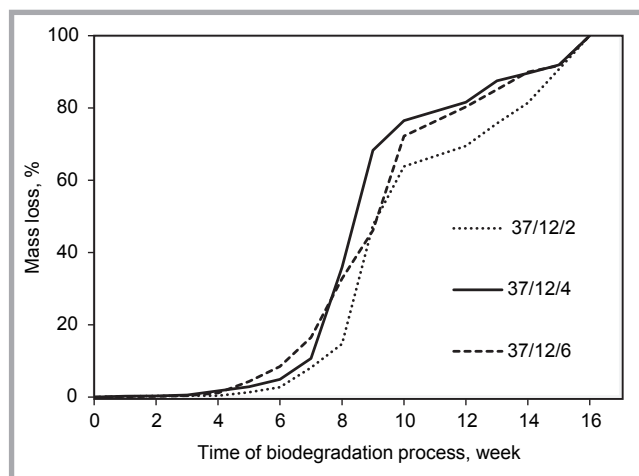
For all samples of PLA agro-nonwovens, the weight average molar masses determined (Mw) were at the same level. The dispersion of results expressed by relative standard deviation (RSD) was below 1%. According to normative guidelines, an RSD up to 5% is permissible for the GPC/SEC method. Also, for all nonwovens tested, similar polydispersity values were obtained, which is a measure of the heterogeneity of the molar mass of polymers. The closer the Mw/Mn ratio is to a value of 1, the less the variation in the chain lengths of macromolecules is (their degree of polymerisation). The polydispersity of the nonwovens tested was in the range of 1.7-1.8, which indicates a small distribution of molar masses. As a result of the polymer processing during the agro-nonwovens manufacturing process, the Mw value decreased by 7.7% in relation to the initial polymer, which indicates a slight hydrolysis of ester bonds. Lowering the molar mass value during polymer processing is a common phenomenon, but should be kept as low as possible.

Table 3 presents the results of tests carried out using the DSC method related to thermal properties of the nonwovens tested.

PLA agrotextiles were subjected to thermal analysis using the DSC technique. The degree of crystallinity was calculated based on the specific melting enthalpy (ΔHm) of the sample tested in relation to that of the 100% crystalline PLA standard (*Table 1*). Analysing the results obtained from thermal tests, it can be seen that the glass transition temperature (Tg) and melting temperature (Tm) are at a similar level (Tg = 57.2-60.1 °C; Tm = 168.0-170.9 °C). Due to the different degrees of crystallinity of the nonwovens, there were differences in the cold crystallisation temperature (Tcc) and cold crystallisation enthalpy (ΔH_{CC}). Along with the increase in the degree of crystallinity, the ordering of the polymer structure increases. A parameter indicating an increase in the polymer crystalline phase is the glass transition temperature, in which there is a change in thermal

Table 2. Average molar masses (M_n, M_w) and polydispersity (M_w/M_n) for initial PLA polymer and PLA agro-nonwovens.

	Sample	M_n, g/mol	M_w, g/mol	M_w/M_n
	PLA polymer	40 400	78 900	1.9
nonwovens	**37/12/2**	41 100	72 800	1.8
	37/12/4	41 200	72 100	1.8
	37/12/6	42 800	73 400	1.7

Table 3. Thermal properties of PLA agro-nonwovens.

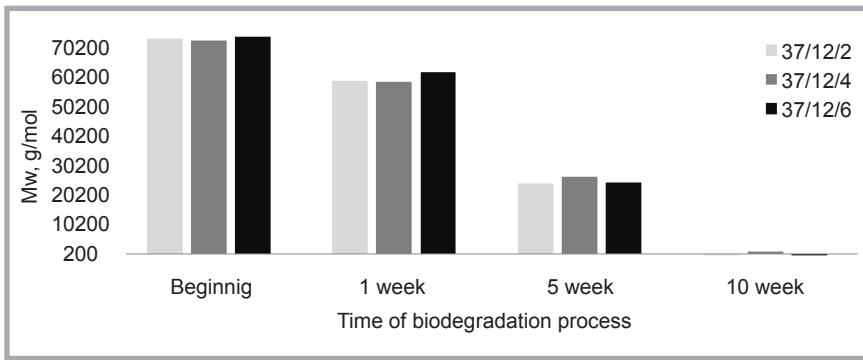| Sample	Thermal analysis					
	T_g, °C	ΔC_p, J/gK	T_{CC}, °C	ΔH_{CC}, J/g	T_m, °C	ΔH_m, J/g
37/12/2	59.8	0.41	90.0	29.8	169.9	40.1
37/12/4	60.1	0.28	86.3	22.6	170.9	42.8
37/12/6	57.2	0.22	79.3	17.7	168.0	46.9

Figure 5. Change in Mw molecular weight of PLA nonwovens during biodegradation.

capacity – the so-called glass transition jump.

Studies on the degradation process of agro-nonwovens made of PLA

Spun-bonded agro-nonwovens made of PLA were subjected to degradation tests under aerobic composting conditions. The total number of microorganisms colonising the inoculum applied was determined as 1.6×10^8 cfu/g. The effect of the duration of the biodegradation process on the mass loss of the samples tested is illustrated in *Figure 4*.

Based on the results of the biodegradability studies, it was observed that after 16 weeks of incubation in compost, the test samples of agro-nonwovens made of

PLA 6252D polymer were completely decomposed. It was found that the crystallinity degree had no effect on the decomposition process of the agro-nonwovens tested in the test medium applied.

Analysis of the kinetics of the degradation (*Figure 4*) shows that three stages of the process can be observed. In the first stage the sample slowly decomposes up to the 7th week of incubation, which is believed to be related to the phase of adaptation and colonisation of microorganism cells on the sample surface. In this stage, according to literature data [7], there is also hydrolytic degradation, which begins with the penetration of water into the structure of the nonwoven and leads to the hydrolysis of ester bonds and the for-

mation of shorter polymer chains, including oligomers as well as monomers.

The second phase we can observe is a rapid increase in sample degradation which lasts up to about the 10th week. This indicates a rapid multiplication of microorganism cells (the degradation graph resembles that of microbial growth kinetics). Literature data provide information that monomers and oligomers dissolved in water are at this stage metabolised by microorganisms present in compost into carbon dioxide and water.

The third phase of degradation is much slower. It is believed that the remnants of the polymer from the test sample in the form of dimers and monomers which are small enough to pass through the semi-permeable bacterial outer membranes are still absorbed by microorganisms and can then be used by them as carbon and energy sources. The sample is further degraded due to metabolic changes [7, 41]. Numerous works are currently underway to find out to which extent soil/compost microorganisms are involved in PLA degradation. Recent studies show that their presence directly intensifies PLA degradation. Also, temperature and substrate conditions are important in this process. Researchers have shown that higher temperatures promote PLA degradation and that compost
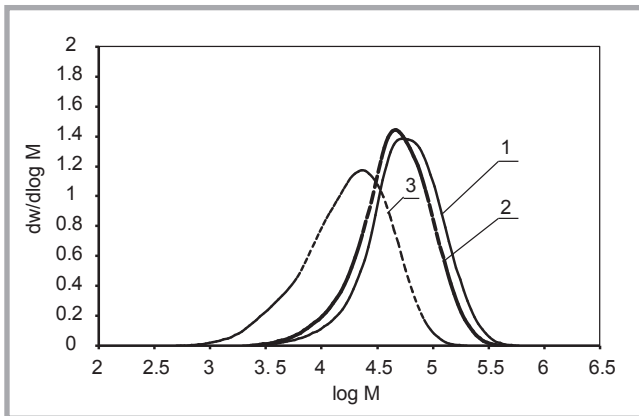

Figure 6. Differential curves of the MMD function for nonwoven 37/12/2 before biodegradation (1), and after 1 week (2) and 5 weeks (3) of biodegradation in compost. After 10 weeks of biodegradation, no polymer was found in the test sample.
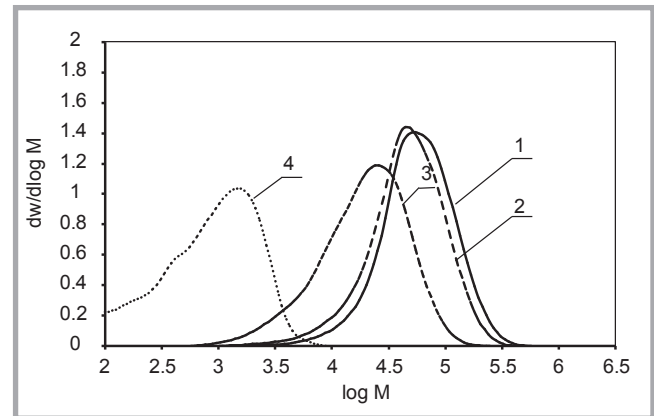

Figure 7. Differential curves of the MMD function for nonwoven 37/12/4 before biodegradation (1), and after 1 week (2), 5 weeks (3) and 10 weeks (4) of biodegradation in compost.

*Table 4. Changes in average molecular mass of PLA agro-nonwovens during biodegradation. Note: * Value below quantification of the detector.*

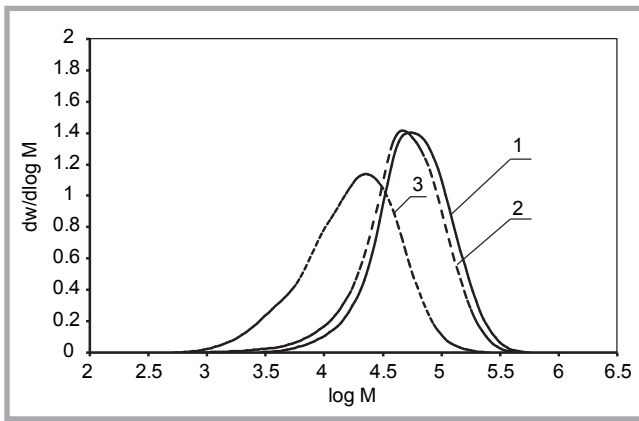| Sample	Duration of biodegradation process, weeks											
	0			1			5			10		
	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
	g/mol			g/mol			g/mol			g/mol		
37/12/2	41 100	72 800	1.8	33 200	58 700	1.8	10 900	23 900	2.2	*	*	*
37/12/4	41 200	72 100	1.8	30 800	58 400	1.9	11 700	26 200	2.2	300	1 100	3.7
37/12/6	42 800	73 400	1.7	32 100	61 700	1.9	10 600	24 500	2.3	*	*	*

Figure 8. *Differential curves of the MMD function for nonwoven 37/12/6 before biodegradation (1) and after 1 week (2) and 5 weeks (3) of biodegradation in compost. After 10 weeks of biodegradation, no polymer was found in the test sample.*
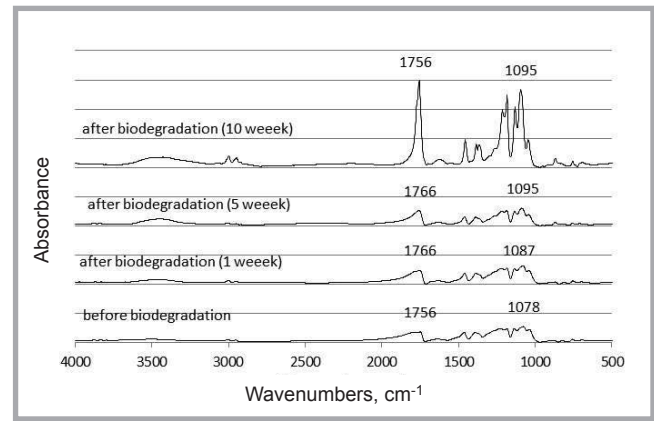

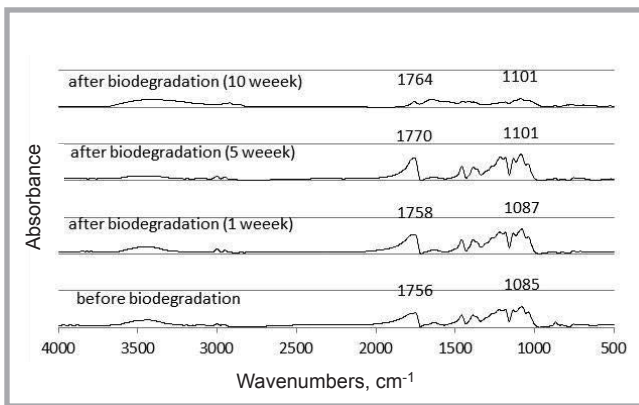**Figure 9.** *FTIR spectra for PLA agro-nonwoven 37/12/2 before and during the biodegradation process.*

Figure 10. *FTIR spectra for PLA agro-nonwoven 37/12/4 before and during the biodegradation process.*
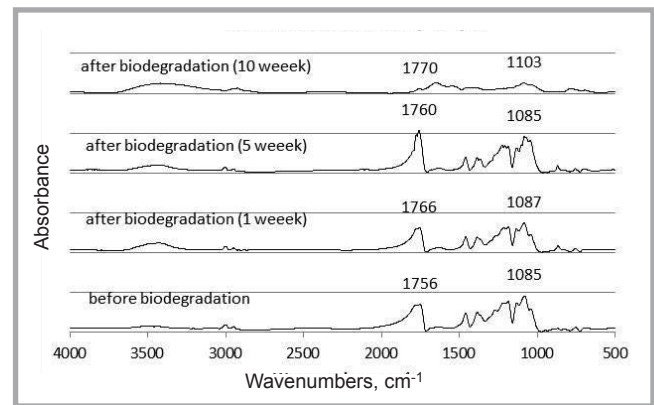

Figure 11. *FTIR spectra for PLA agro-nonwoven 37/12/6 before and during the biodegradation process.*

microorganisms are more active than those found in soil [42].

Agro-nonwovens produced from the above-mentioned polymer were analysed by means of GPC/SEC before as well as after 1, 5 and 10 weeks of the biodegradation process, and the average Mn and Mw molar masses and polydispersity were determined. Molecular characteristics of the samples tested are presented in **Table 4** and **Figures 5-9**.

Based on the results obtained from the GPC/SEC analysis, it was observed that after one week of composting, for all agro-nonwovens, the Mw value had decreased by 17% on average. After 5 weeks of composting, the decrease in the Mw value was 65.5% on average. However, after 10 weeks of incubation for nonwovens marked as 37/12/2 and 37/12/6, no polymer signal was recorded (the lower limit of detectability for the GPC/SEC system is 200 g/mol). For nonwoven fabric marked as 37/12/4, Mw

was determined as 1,100 g/mol. Whilst after 16 weeks, for the 37/12/4 sample no polymer signal was also received. Based on the GPC/SEC analysis, no relationship was found between the degree of crystallinity of the nonwovens and the dynamics of the decrease in their molecular parameters.

Figures 6-8 present differential curves of molecular mass distribution (MMD) functions for PLA agro-nonwovens before and after specific intervals of the biodegradation process.

Selected samples of agro-nonwovens were tested using Fourier transform infrared spectroscopy (FTIR) and oscillatory spectra were obtained, from which the presence of functional groups in the material tested was determined.

Infrared spectroscopy enabled observation of structural changes that occurred during the incubation of the test samples of PLA agro-nonwovens in compost.

Table 5 presents characteristic absorption bands of FTIR spectra for PLA 6252D polymer.

Figures 9-11 show structural changes observed on the basis of IR analysis for spun-bond agro-nonwovens before and

Table 5. *FTIR specific bands for PLA 6252D.*

PLA-specific vibrations	Wavenumbers, cm^{-1}
–CH– stretching	2998, 2947
–C=O ester carbonyl group	1760
–CH– symmetric and asymmetric deformation	1456, 1385, 1362
–C–O– stretching	1269, 1186, 1131, 1094, 1045
–C–C–	873

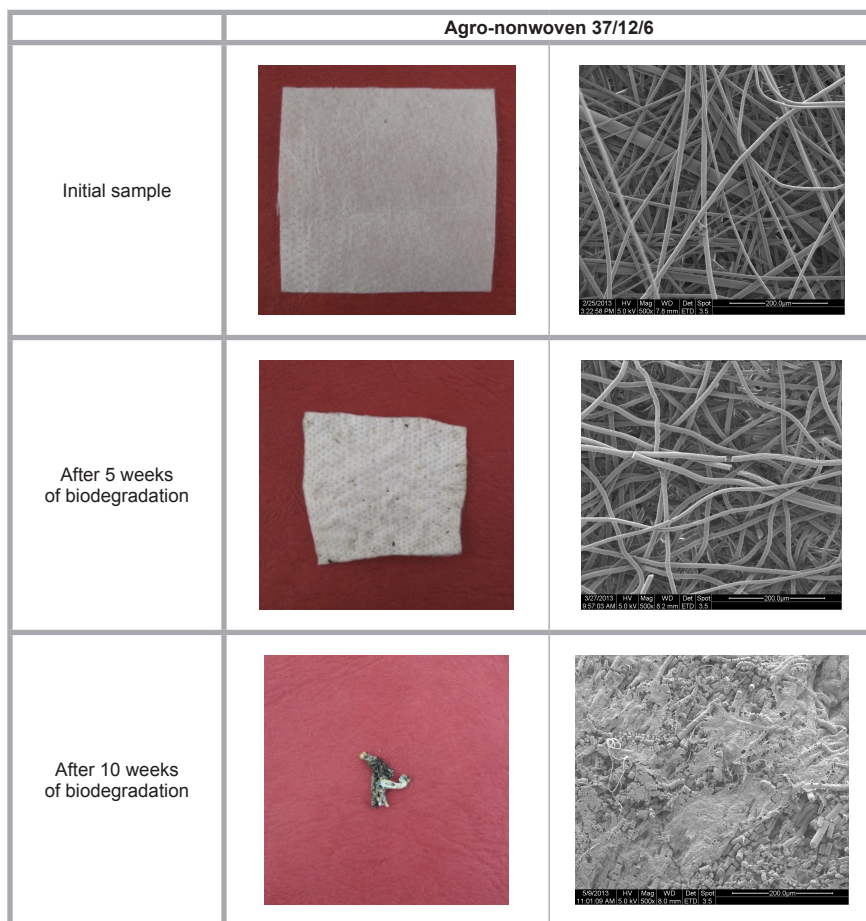|	Agro-nonwoven 37/12/6	
Initial sample		
After 5 weeks of biodegradation		
After 10 weeks of biodegradation		

Figure 12. Changes in the appearance and structure of agro-nonwoven 37/12/6 before and after 5 and 10 weeks of incubation in compost. (SEM images were taken at magnification of 500 times).

after 1, 5 and 10 weeks of the degradation process.

Based on FTIR analysis, the absorbance of PLA ester groups was monitored as a function of the degradation time. As expected, the average percentage of remaining ester groups (% De) in PLA during degradation in compost decreases due to the cleavage of ester groups by hydrolysis, which, according to the author, confirms the degradation of the polymer matrix [44]. Yet more conclusions from the FTIR analysis were drawn by Kalita N.K. et al. [45] Based on the degradation of PLA in compost at 60 °C/58 °C, the authors observed a peak shift from 1750 cm^{-1} to 1758 cm^{-1}, which corresponds to the carbonyl group in the ester. According to the authors, this peak change confirms polymer degradation. After 50 days of the biodegradation process in the FTIR spectra, intensification of the –C–O– stretching band at 1185 cm^{-1} could be observed, whose intensity decreased significantly after 80 days of incubation [45]. An attempt at interpretation of FTIR spectra of PLA

samples was also made by Sedničková M. et al. [46]. According to the authors, after 16 days, degradation in compost at 58 °C had caused a change in the region of valence bands associated with hydroxyl groups, where a wide band was observed with a maximum at 3340 cm^{-1}. As the main process of PLA degradation under natural conditions consists in hydrolysis, the increase in the number of hydroxyl groups during composting is understandable. In contrast, the peaks associated with –CH–(e.g. 1456 cm^{-1}), C=O (at 1752 cm^{-1}), and –C–O–C– groups (between 1132 and 1045 cm^{-1}) do not change throughout the whole IR medium-range region. Apart from the decrease in molar mass, no significant chemical changes were observed using the FTIR technique [46].

Based on FTIR analysis of 37/12/4 and 37/12/6 agro-nonwovens, a decrease in the intensity as a function of the degradation time was observed for PLA-characteristic bands, such as the carbonyl group (–C=O) in the ester moiety of lactide (1760 cm^{-1}) as well as –CO– and

–CH– groups. Also, a wide band with a maximum at 3340 cm^{-1} corresponding to hydroxyl groups was observed. For the agro-nonwoven marked as 37/12/2, a completely different mechanism was observed in the FTIR spectrum: narrowing and increasing the intensity of the peaks for –C=O, and –CO– and –CH– and a wide band with a maximum at 3340 cm^{-1} corresponding to hydroxyl groups. For this nonwoven, after 10 weeks of the degradation process, no peak attributed to the polymer was recorded by the GPC method. During the degradation in compost, biofilm of the microorganisms grows into the surface of the samples. Cell walls of the microorganisms are made of phospholipids and liposaccharides, which contain, among others, –C=O and –CH– moieties, which can theoretically affect the FTIR spectrum. When preparing KBr pellets for IR testing, it is very difficult to separate a polymer sample from degraded nonwoven, and it may possibly be contaminated with biotic material. For all nonwovens tested, however, an increase in the intensity of the peak at 1620 cm^{-1} was observed, which can be attributed to –C=O bonds in the chelate ring closed with an intramolecular hydrogen bond. This type of binding occurs, for example, in hydroxy acids that are formed as a result of PLA degradation. Unfortunately, in scientific publications there are no unequivocal results as for the interpretation of FTIR spectra for poly (lactic acid), which creates space for continuing research in this area.

For the nonwoven samples described in this article, their changes in appearance and structure before and during the degradation process carried out in compost were assessed using a scanning electron microscope (SEM).

Figure 12 presents morphological changes during degradation for the example of sample 37/12/6. Similar results were obtained for the other samples.

■ Conclusions

Spun-bonded nonwovens made of PLA 6252D polymer and marked as 37/12/2, 37/12/4 and 37/12/6 were completely decomposed in simulated laboratory composting during 16 weeks of incubation. The total susceptibility to degradation in compost is also confirmed by observation of changes in appearance and the structure of the samples using SEM.

The degree of crystallinity (11.1-33.6%) and the area density (53.8-56.9 g/m^2) of the agro-nonwovens tested do not affect the dynamics of the degradation process. For the nonwovens tested. the average Mn and Mw molar masses decrease, while the polydispersity increases during the biodegradation process.

The results of the IR test obtained prove that the degradation process affects the structure of the nonwovens made of PLA tested. However, spectrum analysis is ambiguous and difficult to interpret. Unfortunately, based on the literature review, no unequivocal interpretations of the FTIR spectra for biodegraded poly(lactic acid) have been found. In many publications very different spectra and thus extremely different conclusions have been presented. This may create an interesting space for conducting further research in this area.

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Editorial notes

[1] *Examination was made in the accredited Biodegradation Laboratory of Ł-IBWCh (Certificate of accreditation AB 388).*

[2] *Examination was made in the accredited Microbiological Laboratory of Ł-IBWCh (Certificate of accreditation AB 388).*

[3] *Examination was made in the accredited Metrological Laboratory of Ł-IBWCh (Certificate of accreditation AB 388).*

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