Article

Influence of various climatic conditions on the structural changes of semicrystalline PLA spun-bonded mulching nonwovens during outdoor composting

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Abstract: This study analyzed the structural changes of semicrystalline polylactide (PLA) in the form of spun-bonded mulching nonwoven, during outdoor composting. The investigation was carried out at the microstructural, supramolecular and molecular levels using scanning electron microscopy (SEM), wide-angle X-ray diffraction (WAXD) and the viscosity method, respectively. The results showed the varying degree of influence of the climatic condition, prepared compost mixtures and time on the molecular, supramolecular and micromorphological structure of PLA spun-bonded mulching nonwoven and its degradation rate. The obtained experimental results revealed how the popular outdoor composting method, realized under two different European climatic conditions (in Poland and in Bulgary), affects the degradation of PLA nonwoven, designed for agriculture use.

1. Introduction

In recent years, with regard to the environmental preservation and according to the circular economy, novel biodegradable materials, made from biomass waste for application in many areas of life, were developed [1, 2]. The group of biopolymers that has attracted considerable attention includes poly(lactic acid) or polylactide (PLA) [3]. These are synthesized from completely renewable sources, for example corn, possess excellent mechanical properties, which are comparable with those of other polyesters, and can be used for compost or biodegradation [4].

The synthesis of PLA, depending on its application, is based on the polycondensation of lactic acid or the ring-opening polymerization of lactide (LA) obtained from the depolymerization of oligomers of lactic acid (2-hydroxypropionic) (LAc). LAc is synthesized of hydrocarbons of agricultural origin, such as biomass waste, by means of a fermentation process with the use of bacteria Lactobacilli. The polymerization of lactide is usually initiated by covalent alcoholates (Mt(OR)n), and results in polylactide composed of macromolecules with ester and hydroxyl terminal groups, respectively [5]. The presence of various stereoisomeric lactide forms, different chirality in the polymer chain, and the creation of different supramolecular structures of polymers strongly influence the physical properties of the final products [6-8].

The poly(L-lactide) homopolymer is a crystallizable polymer and can crystallize in three different polymorphous-ordered forms: α [9], β [10], γ [11], one disorder form α' [12, 13] and *meso*-phase [14] characterized by different properties [15]. In the technological regime, where poly(L-lactide) is usually applied with low content (<10%) of D-lactide isomers, the main observed crystalline structure form is α' which ensures the optimum usable properties of final materials [16, 17].

PLA is also well known as hydrolysable and unstable biodegradable polyester [18, 19]. Degradation of this aliphatic polyester depends on the physical, chemical and biological agents, mainly through hydrolytic or thermal degradation. [20-22]. The degree and rate of degradation also depends on the molecular and supramolecular structures of the polymer [23-25]; however, current knowledge is based on the experiments carried out mainly on the amorphous PLA materials degraded under laboratory or natural conditions [26, 27]. The presented results from composting tests have demonstrated that materials made from PLA can be degraded after several weeks. However, the temperature of the compost must be near or above the glass transition temperature, which for PLA is in the range of 55 – 65°C [28, 29]. The degradation of PLA products in outdoors manure piles is slower in a Mediterranean climate [30].

The advantages of PLA have made it a polymer with huge application potential in agriculture in the form of packaging [31], strings [32] and nonwoven fabrics for mulching [33, 34]. Due to these potential applications, it is important to carry out investigation related to the testing of the degradation of prototypes of PLA products during composting under conditions typical for agriculture and horticulture—this has become the motivation to carry out the experiment described in this work.

In this study, degradation in an outdoor regime was investigated which is interesting not only from the scientific point of view. The possibility of utilizing plastics by composting in a home is extremely important with respect to environmental protection, and could be a method of waste reduction. Semicrystalline PLA in the form of spun-bonded nonwoven, such as the material applied to mulching plants in summer 2015, was composted in soil with peat with and without the addition of a commercially available agent for compost containing nitrogen, Radivit®, under two different climatic conditions, defined according to Köppen–Geiger's classification as humid continental (Dfb) and humid subtropical (Cfa) [35]. Additionally, a part of the composting prism was covered by foil which is a typical method used in horticulture and agriculture to accelerate the composting process. The experiment was carried out from April 10, 2015 to October 10, 2017. The effects of degradation were analyzed by using scanning electron microscopy (SEM), wide-angle X-ray diffraction (WAXD) and the viscosity method, which provided information about structural changes at the microstructural, supramolecular and molecular levels, respectively.

. Materials and Methods

2.1. Materials

The studied materials were made from the poli(L-lactide) which contained 1,4% of D-lactide, Nature Works 6202D (Cargill Dow, USA), with the addition of black dye (PolyOne, USA). The PLA spun-bonded mulching nonwovens with a mass per unit area of 50.1, g/m^2 were performed by using the large laboratory stand. The methodology guaranteed optimal mechanical properties with the semicrystalline structures what were previously described [36].

2.2. Composting condition and method

The outdoor composting was realized at two experimental stations: Vegetable Experimental Station of the University of Agriculture in Krakow, Poland (50º04′N, 19º51′E) and Agroecological Centre (AEC) at the Agricultural University of Plovdiv, Bulgaria (42°09′N 24°45′E) where the climate is, according to Köppen–Geiger's classification, humid continental (Dfb) and humid subtropical (Cfa), respectively [37]. The experiments were started on the last day of June 2014 through the deposition of nonwoven strips on the soil, which were supposed to imitate the litter in contact with

the soil. On the last day of August, the litter nonwoven strips were cut into 5x5 cm² pieces and added to the compost prisms of the following most popular composting mixtures:

- Soil with peat (sample notation is defined as S+P)
- Soil with peat and a commercially available agent for composting which contains nitrogen, Radivit® (sample notation is defined as S+P+R)

Additionally, part of the compost prisms was covered with foil and that sample is defined as S+P+F and S+P+R+F, respectively. The samples for testing were taken after 1 year and 2 years of composting.

2.3. SEM method

The effect of degradation on the change of spun-bonded nonwoven morphology was observed under a scanning electron microscope (SEM) (Nova NanoSEM 230). The studies were carried out by the use of a Low-Vacuum environment and beam energy 10 keV.

2.4. Molecular weight

Molecular weight was measured by the viscosity method in a diluted polymer/dichloromethane (0.08 g/dL) using an Ubbelohde viscometer (Type 2a.) at 25°C. The viscosity-average molecular weight, $M\eta$, was then calculated from the intrinsic viscosity *[η]* by using the following equation [38]:

$$[\eta] = K M_\eta{}^\alpha \tag{1}$$

where K and α are constants which equal PLLA 5.45×10^{-4} and 0.74, respectively.

2.5. DSC method

The thermal properties of the studied materials were analysed using a model Q 2000 differential scanning calorimeter, model Q 2000 (TA Instrument Inc., UK), in the range of 0 - 250°C at a heating rate of 10°C/min.

2.6. WAXDmethod

Measurements of the crystalline structure of PLA were carried out by means of a diffractometer X'Pert PRO (PANalytical, Netherland) with the use of CuKα source (λ= 0.154 nm) and the following parameters: accelerating voltage 40 kV; anode current density 30 mA. A semiconductor counter X'Celector was used as a detector. Diffraction patterns for powdered samples were taken within the range of angles of 2θ: 5° - 45°.

3. Results and Discussion

3.1. Analysis of micromorphology

In the first part of the evaluation of the degradation of PLA spun-bonded mulching nonwovens, the influence of the degradation factors such as time, climatic conditions and composition of compost on the physical microstructure of the nonwoven fabrics was analysed. Due to the strong diffusion of the soil inside the nonwoven structure and its difficulty with purification, a reliable assessment of the weight loss was not possible. Thus, in this work, changes at the microstructure level were assessed as an investigation of the physical structures of nonwovens, by means of scanning electron microscopy. Figure 1 presents the SEM images recorded before and after degradation in magnification ×1600. It is clearly shown that the results of the composting process are characteristic transverse cracks of fibres after just one year of degradation [39]. Additionally, in the case of composting in a humid subtropical climate, the preliminary fragmentation of fibers is also observed. After the second year of composting, all of the studied samples are partially fragmented; however, there is a lack of visible fragmentation to the powdered form. Based on the presented results, it can be concluded that the degradation process after two years is still in its early stages at the micromorphology level. The materials have partially fragmented what would be called

disintegration without any visible typical effects of fragmentation and mineralization [40]. Moreover, it can also be assumed that changes in micromorphology are slightly more severe when composting is carried out in a humid subtropical climate. In addition, it cannot be determined which compost composition has a more degrading effect on semicrystalline PLA spun-bonded mulching nonwovens based on SEM images of micromorphology (Figure 1). The investigation at the microstructural scale of the effects of degradation also demonstrated an insignificant influence of covering the compost prism with foil on the destruction and fragmentation of studied samples, mainly visible as surface defects. Based on the assessment of changes in the microstructure of PLA nonwovens, it can be concluded that composting of semicrystalline polymer material under natural conditions is not trivial. Without the proper temperature, soil moisture and natural microorganisms are not sufficient conditions for the rapid degradation of the semicrystalline form of PLA.
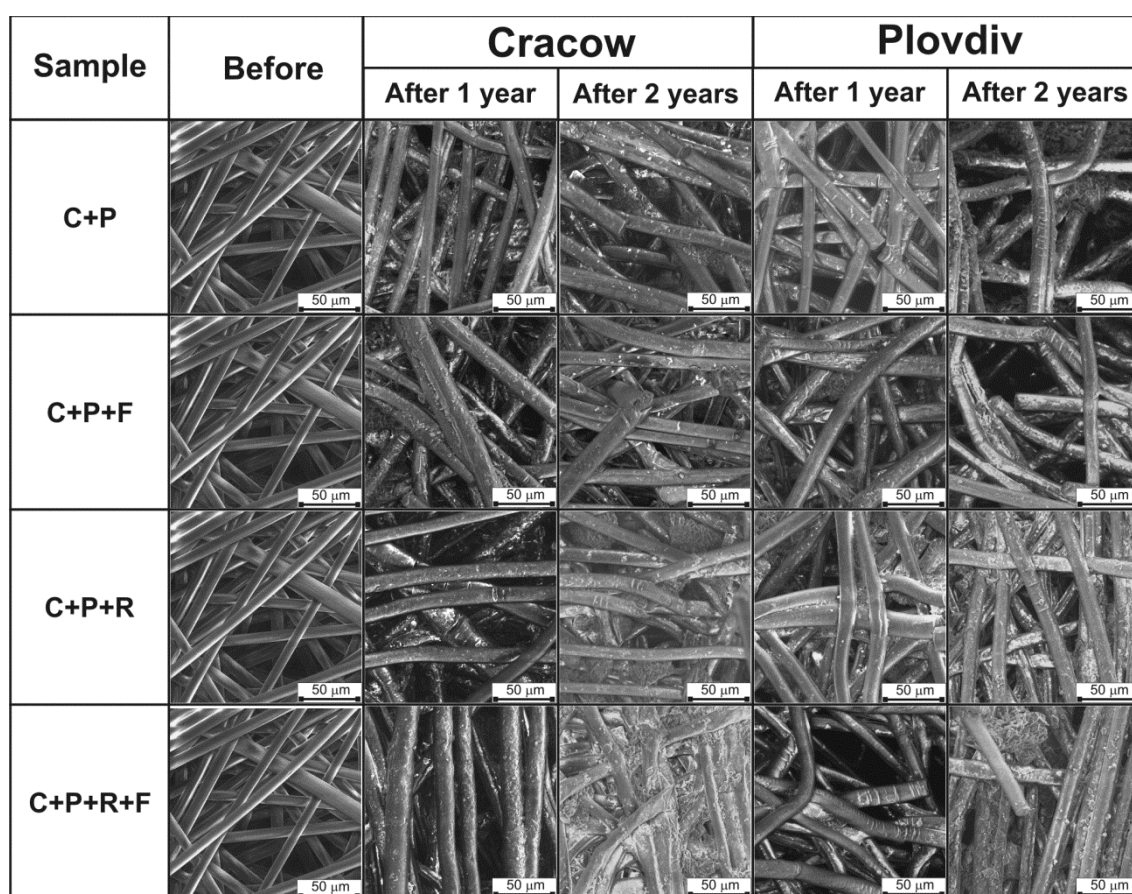

Figure 1. SEM images of PLA spun-bonded nonwovens before and after composting in various conditions.

3.2. Molecular weight analysis

Figure 2 presents the changes in PLA-estimated intrinsic viscosity and calculated viscosity-average molecular weight that resulted from various composting mixtures and times. The one-year composting process of nonwovens in selected conditions did not significantly change the viscosity-average molecular weight of the PLA. The $M\eta$ decreased from 38.8 kDa to 37.7–38.0 kDa and 37.0–37.2 kDa in the case of composting in soli and composting in soli with Radivit® covered with foil, respectively. The changes in $M\eta$ are more visible after the second year of composting. Moreover, after two years of the composting process, the influence of climatic condition on the calculated viscosity-average molecular weight is more visible. According to the presented result, as expected, the most intensive changes in $M\eta$ parameters are observed in the case of the composting process in the humid subtropical climate (Cfa). After a year of composing, the calculated $M\eta$ for samples composting in Plovdiv decreased from 38.8 kDa to 31.9–33.0 kDa, while for the samples composting in Cracow $M\eta$ decreased to only 35.0–34.4 kDa. It is worth noting that the composting

process in outdoor conditions—where the maximum temperatures in the composting prism during the experiment were in the case of Cracow in the rage of 25–32°C, and in the case of Plovdiv in the range of 28–35°C—affected the molecular structure of the polymer, but the effects of degradation are not as significant as in the case of laboratory tests or degradation realized in the municipal composting heap, where the temperatures are in the range of 56–65°C [29]. The presented results confirm the significant importance of the supplied energy in the form of heat as a degrading factor, which is possible to obtain under natural conditions by changing the climate zone or providing heat from an artificial source. Adding Radivit® agent and covering the composting prism with foil insignificantly accelerate the degradation of semicrystalline PLA material at the molecular level, which is a significant observation from the perspective of PLA degradation in natural conditions. In summary, the obtained results of molecular weight changes correlate with changes at the microstructure level and confirm that after two years of composting PLA nonwoven in natural conditions, degradation is visible but it is still at a preliminary stage.
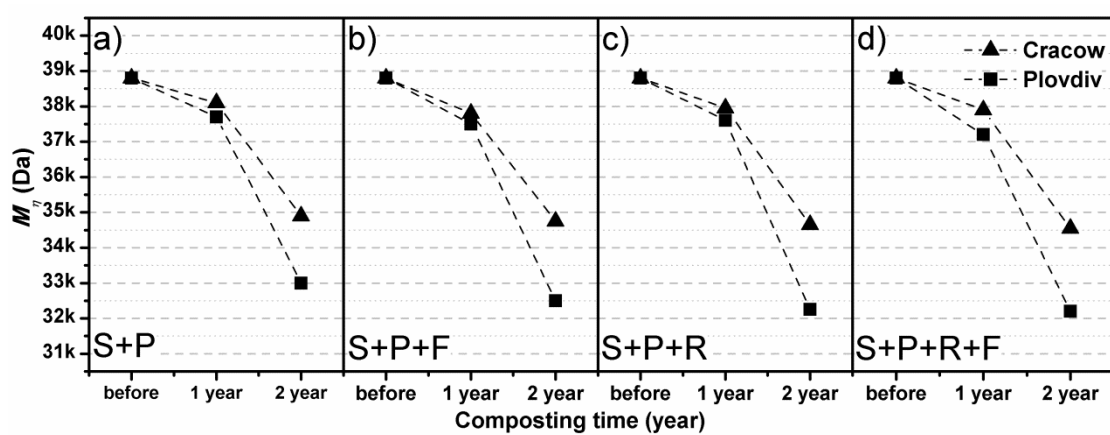
Figure 2. The changes in viscosity-average molecular weight of PLA during composting in: **(a)** soil with peat, **(b)** soil with peat covered with foil, **(c)** soil with peat and Radivit®, and **(d)** soil with peat and Radivit® covered with foil.

3.3. DSC results

Analysis of the PLA spun-bonded mulching nonwoven thermal properties was performed before and after composting in various media and climate conditions.

In Figure 3, the first heating DSC thermograms of the studied materials are presented. Figure 4 compares the estimated variation of the heat capacity (ΔCp) and degree of crystallinity (χ_c) for each studied PLA sample. The degree of crystallinity was calculated using the following equation:

$$\chi_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{100\%}} \times 100\% \qquad (2)$$

where ΔH_m is the melting enthalpy, ΔH_{cc} is the cold crystallisation enthalpy and $\Delta H100\%$ is the melting enthalpy of 100% crystalline PLA, which is equal to 93.1 J g^{-1}[41].

On all of the thermograms, the melting point of PLA around 166°C is clearly visible. The analysis of determined values shows the slight decrease in T_m of the studied samples mainly after 2 years of composting from 166.5°C to 166.0°C. This is an interesting observation because it suggests that most of the crystallites detected by DSC originate from the locally ordered structure obtained during degradation. This phenomenon will be the subject of WAXD studies, the results of which are presented later in this work.

More clearly visible changes in the thermal properties of studied samples were noted for the glass transition point and cold crystallization peak. For the samples composted in the humid subtropical climate, a decrease in T_g and T_{cc} was discernible, and its range depended on the composting mixture and the presence of a foil cover (Figure 3b). In samples composting for 2 years, an insignificant or no cold crystallization peak was noted with the significant decrease in the glass transition point. These results correlate with the results of molecular weight analysis estimated by the viscosity method.

The glass transition point and cold crystallization peak are observed at a lower temperature for the polymer with a lower viscosity-average molecular weight. This phenomenon is evident because the polymer with lower $M\eta$ requires lower thermal energy to transition from a solid to a glassy form. The decrease in molecule weight also results in an insignificant decrease in the cold crystallization point (Figure 3).
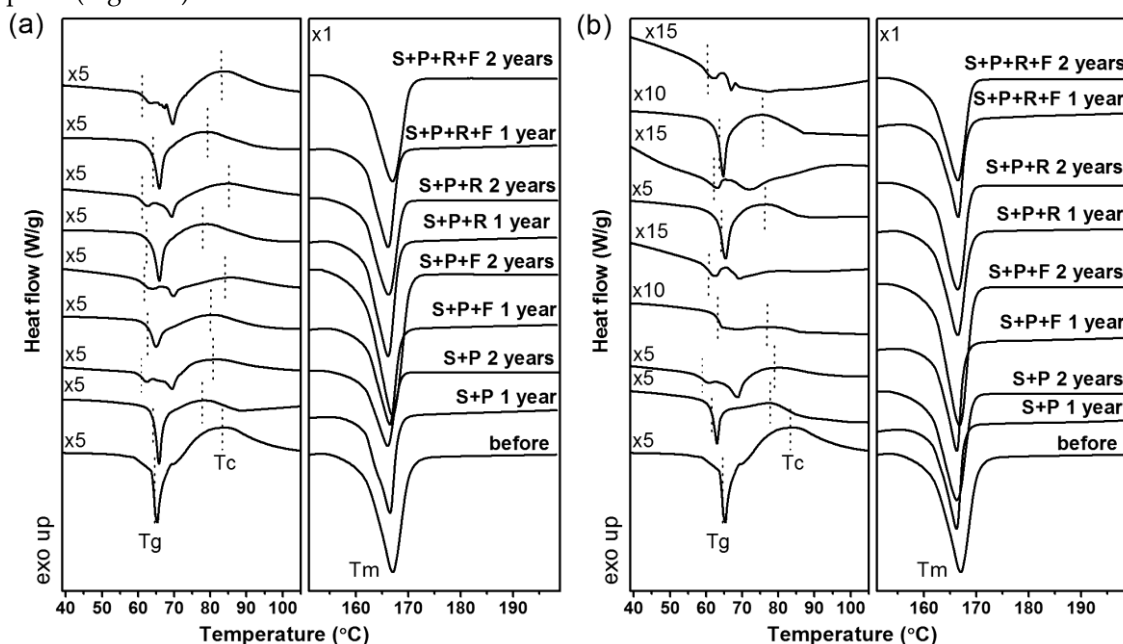
Figure 3. DSC thermographs of PLA spun-bonded mulching nonwovens recorded before and after composting in **(a)** Cracow and **(b)** Plovdiv.

The composting process changes the thermal properties of the studied sample. This is mainly observed as a decrease in the values T_g and T_c, but also changes in the supramolecular structures of the polymer. In Figure 4, the variation in the heat capacity and degree of crystallinity is presented as a function of degradation time. The increase in χ_c with decreasing ΔC_p is clearly presented. According to the presented results of the numerical analysis of the obtained DSC thermograms, the influence of climatic condition on the PLA degradation is visible. The increase in the degree of crystallinity with the decreasing variation of the heat capacity is more intense when composting was conducted in a Cfa climate than in a Dfb climate. Moreover, composting with the use of a foil cover contributes to the occurrence of significant structural changes in the polymer in a shorter time, which is clearly visible in the case of samples S+P+F and S+P+R+F. Additionally, the obtained DSC results suggested that the addition of Radivit® to the composting mixture causes an insignificant increase in the velocity of structural changes of PLA during degradation, observed as an increase in the degree of crystallinity with the decreasing variation of the heat capacity, as shown in the viscosity-average molecular weight analysis results.
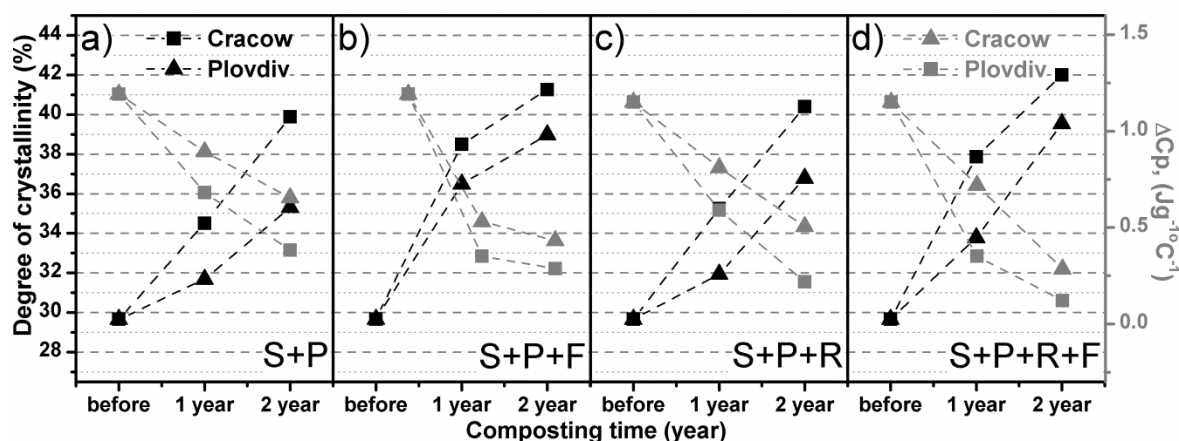
Figure 4. Results of DSC analysis of semicrystalline PLA spun-bonded mulching nonwoven before and after composting in: **(a)** soil with peat, **(b)** soil with peat covered with foil, **(c)** soil with peat and Radivit®, **(d)** soil with peat and Radivit® covered with foil.

3.4. WAXD results

In Figure 5, X-ray diffractograms of investigated semicrystalline PLA mulching nonwoven, before and after composting, are compared. In all of the obtained diffractograms, two dominant diffraction peaks located at 2θ, equal to 16.5° and 18.8°, are clearly visible, corresponding to (110)/(200) and (203) lattice planes of α or α' forms of PLA. In addition, for the composted samples, a sharp diffraction peak at around 2θ, equal to 22°, 27° and 28°, and many weak visible diffraction peaks in the range of 2θ 10°–40°, assigned to the reflection from crystallographic planes of soil, are also discernible.
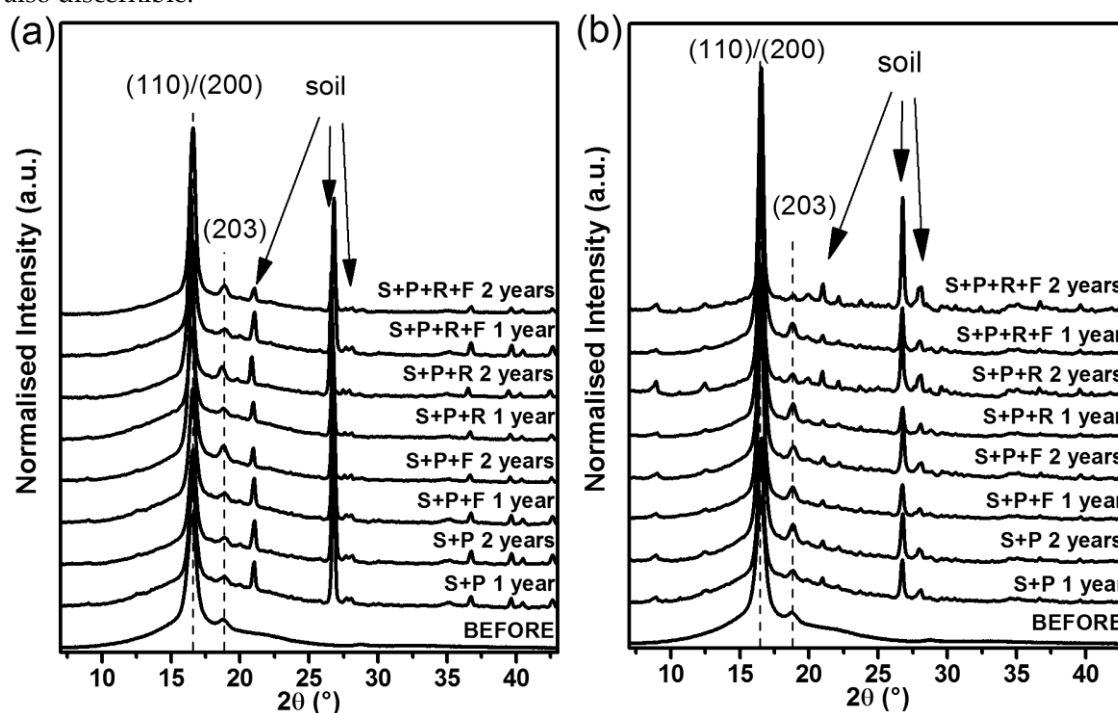
Figure 5. WAXS diffractograms of PLA spun-bonded mulching nonwovens before and after composting in **(a)** Cracow and **(b)** Plovdiv.

The visible increase in PLA diffraction peak intensity suggested significant supramolecular changes in the studied polymer. This was analysed in depth by the deconvolution of the diffractograms into the amorphous halo and the crystalline peaks. For this analysis, the experimental data were fitted by a broad Gaussian peak, characteristic of the amorphous component, and main narrow Gaussian–Lorentzian peaks relevant to the crystalline form, all calculated using the

WAXSFIT software based on Hindeleh and Johnson's method [42]. The shapes of the crystalline peaks and the amorphous halo were matched according to the model proposed by Stoclet et al [43]. The crystalline phase contents in the studied materials were calculated according to the following equation:

$$\chi_c = \frac{A_C}{A_C - A_A} \times 100\%$$

(3)

where A_A and A_C are the integral intensities of the amorphous halo and the peaks originating from the crystalline phase, respectively.

Another characteristic feature of the structure formed after composting of semicrystalline PLA spun-bonded nonwoven, under various conditions, was detected by an analysis of the d-spacing (lattice length) calculated according to Bragg's equation:

$$d_{(hkl)} = \frac{\lambda}{2 \sin \theta}$$

(4)

where λ is the wavelength of the X-ray source (0.15418 nm) and θ is an angle of the reflection (half of 2θ of peak position).

Figure 6 presents the results of numerical analysis of recorded WAXD diffractograms. The degrees of crystallinity estimated by the WAXD method and d-spacing calculated for the two strong visible diffraction peaks corresponding to (110)/(200) and (203) lattice planes, as a function of degradation time, are similar to those estimated by the DSC method. The degradation of the amorphous phase during composting, along with the ordering of the crystalline phase, caused visible changes in the shape of diffractograms as well as an increase in the determined numerical method of the degree of crystallinity. The influence of the four degradation factors—time, climatic conditions, composting mixtures and covering with foil—on the crystallisation of the studied sample is clearly presented. The χ_c is higher and d-spacing is lower in the case of composting in a Cfa climate than in a Dfb climate. What is more, covering composting prisms with foil allows faster degradation and crystallization after the first year of conducting the experiment, which is clearly visible in the case of composting under the Dfb climatic condition. Additionally, the addition of Radivit ® to the composting mixture causes an insignificant increase in the velocity of structural changes of PLA during degradation, observed as an increase in the degree of crystallinity and decrease in d-spacing. The obtained results testify that the degradation of PLA is not only detectable as an increase in crystallinity but also as the ordering of crystalline forms. For the uncomposted nonwoven, the mean values of the d-spacings were 0.537 nm and 0.474 nm for the (110)/(200) and (203) lattice planes, respectively. The calculated cell units were equal to a=1.074 nm, b=0.620 nm, and c=3.018 nm. For the nonwoven composted in the soil with peat and Radivit® under the Cfa climatic condition, the diameters of the lattice changed, and the mean d-spacings were approximately 0.533 nm and 0.469 nm (a=1.066 nm, b=0.615 nm, and c=2.961 nm). In sum, the initial disorder α' crystalline form of the studied material is ordering to the α form of PLA during composting.
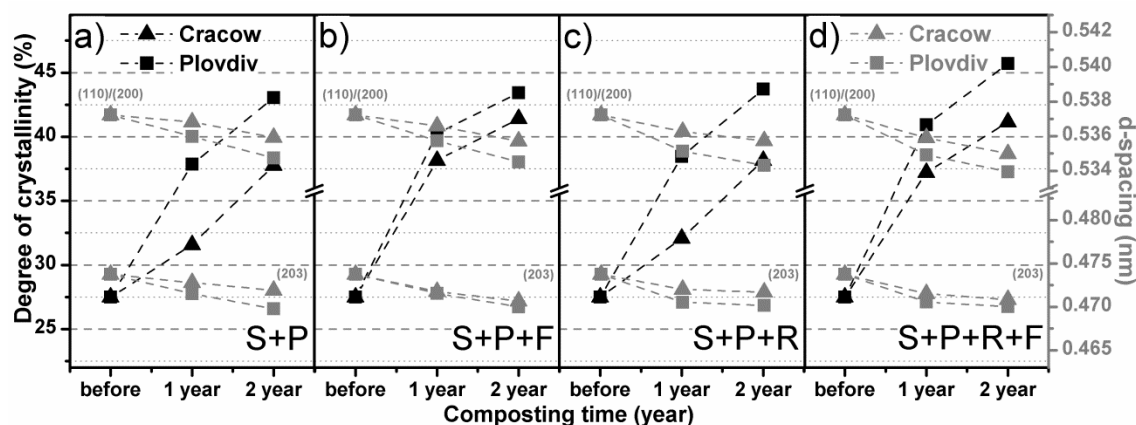
Figure 6. Results of numerical analysis of WAXD diffractograms recorded for PLA spun-bonded mulching nonwovens before and after composting in: **(a)** soil with peat, **(b)** soil with peat covered with foil, **(c)** soil with peat and Radivit®, **(d)** soil with peat and Radivit® covered with foil.

3. Conclusion

An investigation of the structural changes of PLA spun-bonded mulching nonwovens after two years outdoor composting revealed important information about the degradation of semicrystalline PLA and significantly increased the scientific knowledge about this polymer. The most important conclusions include the following:

1. Degradation of semicrystalline PLA materials by the outdoor composting method in various climatic conditions for one year is not efficient, as confirmed mostly by SEM studies. An increase in the degree of crystallinity with decreasing viscosity-average molecular weight and changes in the thermal properties of the studied material are observed but to a lesser extent than after composting for two years.
2. The climatic condition and the presence of a foil cover on the composting prism are important for the rapid degradation of semicrystalline PLA by the outdoor composting method. Ensuring high average annual temperatures, preferably close to the glass transition temperature of PLA, and ensuring its stability are crucial from the point of view of composting semicrystalline PLA materials.
3. The addition of a commercially available agent that contains nitrogen (Radivit®) to the composting mixture slightly accelerates the degradation process, but not as much as the climatic conditions and covering the composting prism with foil.
4. Outdoor composting had a strong effect on the disorder-to-order phase transition (α' to α form) of PLA. The decrease in d-spacing measured for the most intense WAXD diffraction peaks is observed after the first year of degradation and is more pronounced after two years of conducting the process. On the basis of the obtained results, it can be assumed that, in the case of PLA degradation, changes in d-spacing and the disorder-to-order phase transition of PLA could be precise degradation assessment indicators.

Author Contributions: Michał Puchalski designed the analytical part of experiment, performed the WAXD, DSC and SEM measurement, analyzed all experimental data and wrote the paper; Piotr Siwek designed the composting of materials and performed the composting in Cracow; Nicolay Panayotov and, Małgorzata Berova co-designed the composting of materials and performed the composting in Plovdiv; Stanisława Kowalska performed mass loss and molecular weight changes measurements, Izabella Krucińska co-designed the analytical part experiment and contributed to wrote the paper, was the leader of Biogratex Project.

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